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XIV. *On the Theory of Illumination in a Fog.*

By Lord RAYLEIGH, *F.R.S.**

As a step towards a better understanding of the action of fog upon light, it seems desirable to investigate what the phenomena would be in the simplest case that can be proposed. For this purpose we may consider the atmosphere and the material composing the fog to be *absolutely transparent*, and also make abstraction from the influence of obstacles, among which must be included the ground itself.

Conceive a small source of radiation, *e. g.* an incandescent carbon filament, to be surrounded by a spherical cloud, of uniform density, or at any rate symmetrically disposed round the source, outside of which the atmosphere is clear. Since by hypothesis there is no absorption, whatever radiation is emitted by the source passes outward through the external surface of the cloud. The effect of the cloud is to cause diffusion, *i. e.* to spread the rays passing through any small area of the surface (which in the absence of the cloud would be limited to a small solid angle) more or less uniformly over the complete hemisphere.

Whether the total radiation passing outwards through the small area on the external surface of the cloud is affected by

* Read April 25, 1885.

the existence of the cloud depends upon the circumstances of the case. If it be laid down that the total emission of energy from the source is given, then the presence of the cloud makes no difference in respect of the energy passing any element of the spherical area. But this supposition does not correspond to a constant temperature of the source, in consequence of the energy received back from the cloud by reflection. To keep the total emission of energy constant, we should have to suppose a rise of temperature increasing indefinitely with the size and density of the cloud.

Let us now suppose that the region under consideration is bounded upon all sides by a distant envelope of perfect reflecting-power. Then, whatever the density of the clouds which may wholly or partially occupy the enclosure, we know, by the second law of thermodynamics, that at every internal point there is radiation in every direction of the full amount corresponding to the temperature of the source. In one sense this conclusion holds good, even although the matter composing the cloud has the power of absorption. But in that case equilibrium would not be attained until the clouds themselves to the remotest parts had acquired the temperature of the source; whereas under the supposition of perfect transparency the temperature of the cloud is a matter of indifference; and equilibrium is attained in a time dependent upon that required by light to traverse the enclosure. So far we have made no supposition as to the distribution of the cloud; but we will now imagine a layer of such thickness as to allow only a very small fraction of the incident radiation to penetrate it, to line the interior of the reflecting envelope. This layer itself plays the part of a practically perfect reflector; and it is not difficult to see that the reflecting envelope hitherto conceived to lie beyond it may be removed without interfering with the state of things on the inner side of the layer of cloud. We thus arrive at the rather startling conclusion that at any distance from the source, and whatever the distribution of clouds, there is always in every direction the full radiation due to the temperature of tho source, provided only that there lie outside a complete shell of cloud sufficiently thick to be impervious. And this state of things is maintained without (on the whole) emission of energy from the source.

Even if the material composing the cloud possesses absorbing-power for some kinds of radiation, *e. g.* for dark radiation, but is perfectly transparent to other kinds, *e. g.* luminous radiation, the general theorem holds good as respects the latter kinds; so that in the case supposed the light would still be everywhere the same as in a clear enclosure whose walls have throughout the same luminosity as the source. But in order to compensate the absorption of dark rays, the source must now be supplied with energy.

Some of the principles here enunciated have an acoustical as well as an optical application, and indeed first occurred to me some years ago in connection with Prof. Tyndall's investigations upon fog-signals. The effect of "acoustic clouds" analogous to fog (and unattended with absorption of energy), might be very different upon the report of a gun and upon the sustained sound of a siren, the latter being reinforced by reflection from the acoustic fog.

The theory presented in the present paper may be illustrated by the known solution of the comparatively simple problem of a pile of transparent plates*. If ρ denote the proportion of the incident light reflected at a single surface, then the proportion reflected $\phi(m)$, and transmitted $\psi(m)$, by a pile of m plates is given by

$$\frac{\phi(m)}{2m\rho}=\frac{\psi(m)}{1-\rho}=\frac{1}{1+(2m-1)\rho}.$$

From these expressions it is evident that, however small ρ may be, *i. e.* however feeble the reflection at a single surface, we have only to suppose m large enough in order that the reflection may be as complete, and the transmission as small, as we please. Such a pile may, under ordinary conditions, be regarded as impervious.

But now suppose that after passing the pile of m plates, the light is incident upon a second pile of n plates, and consider the intensity between the two piles, the original intensity being unity, as before. For the intensity of the light travelling in the original direction we have

$$\psi(m)+\psi(m)\,.\,\phi(n)\,.\,\phi(m)+\psi(m)\,.\,\{\phi(n)\,.\,\phi(m)\}^2$$
$$+\psi(m)\,.\,\{\phi(n)\,.\,\phi(m)\}^3+\ldots\,;$$

* Stokes, Proc. Roy. Soc. vol. xi. p. 545 (1862).

or on summation of the geometric series,

$$\frac{\psi(m)}{1-\phi(n)\cdot\phi(m)}.$$

If we introduce the values of ϕ and ψ in terms of m, n, ρ this becomes

$$\frac{2n\rho+1-\rho}{2(m+n)\rho+1-\rho}.$$

In like manner, for the light going the other way we have

$$\frac{\phi(m)\cdot\phi(n)}{1-\phi(m)\cdot\phi(n)};$$

or in terms of m, n, ρ,

$$\frac{2n\rho}{2(m+n)\rho+1-\rho}.$$

When m and n are great, both expressions reduce to $n/(m+n)$; so that the light passing in the two directions is equally bright. Moreover, and this is the point to be especially noticed, however great m may be—that is, however impervious the first pile is, the light between the two piles may be made to approach the original light in brightness as nearly as we please, by sufficiently increasing the number of plates in the second pile; that is, the light between the piles may be made to be the same as if the first pile were removed. From this example we may understand more clearly how a very small quantity of light penetrating directly may be beaten backwards and forwards, as between two reflectors, until the original intensity is recovered.

XV. *A Monochromatic Telescope, with Application to Photometry.* *By* Lord Rayleigh, *F.R.S.**

The purpose of this instrument is to exhibit external objects as they would be seen either with the naked eye, or through a telescope, if lighted with approximately monochromatic light; that is, to do more perfectly what is done roughly by a coloured glass.

The arrangement is not new, though I am not aware that it has ever been described. In 1870 I employed it for deter-

* Read April 25, 1885.

minations of absorption, and, if my memory serves me right, I heard soon afterwards from Clerk-Maxwell that he also had used it. It is, indeed, a very slight modification of Maxwell's colour-box.

In the ordinary form of that instrument, white light admitted through a slit is rendered parallel by a collimating lens, dispersed by flint-glass prisms, and then brought to a focus at a screen, upon which accordingly a pure spectrum is formed. This screen is perforated by a second slit, immediately behind which the observer places his eye. It is evident that the light passing the aperture is approximately monochromatic, so that the observer, if he focuses his eye suitably, will see the prism illuminated with this kind of light. The only addition now required to convert the instrument into a monochromatic telescope is a lens placed just within the first slit, of such power as to throw an image of external objects upon the prism or diaphragm upon which the eye is focused. If desired, an eye-lens may be placed at the second slit; but this is not generally needed.

In the present instrument a direct-vision dispersing prism is used, so that the optical parts can be all disposed in a narrow box of nearly 3 feet in length. The lenses are all single lenses, and work sufficiently well. The slits are of such width that either coincides with the image of the other, and their relative position is so chosen that the mean refrangibility of the light is that corresponding to sodium. Objects seen through the instrument thus appear as if lighted by a sodium flame.

The principal object which I had in view in the construction of the instrument now exhibited was to see whether it could be made of service in the comparison of compound lights of somewhat different colours—a problem just now attracting attention in connection with electric lighting. It is scarcely necessary to say that a comparison of this kind is physically incomplete unless it extends to all the spectral components separately; but for commercial purposes such an extended comparison is too complicated, and indeed useless. Determinations at two points of the spectrum, as proposed by Capt. Abney, would certainly suffice for ordinary purposes; and in view of the convenience of expressing the result by a

single number, it is not unlikely that people practically concerned in these matters will content themselves with a comparison at one point. It seems desirable that some convention should be arrived at without much further delay; so that two lights should be considered to be commercially equal, if they have the same intensity of, *e. g.*, sodium or of thallium light. It will be understood that such a mode of estimation assumes that the intensity varies along the spectrum in a gradual manner; and this consideration may tell against the use of the sodium light as a standard, inasmuch as the component in question often predominates unduly in candle-flames from the actual presence of sodium.

Whatever choice be made, an instrument like the present may be employed to make the desired selection; and it is applicable to any photometric arrangement. For my own experiments I have used the shadow-method, and find it possible to compare any bright sources, however different in colour. The only difficulty arises from the necessary enfeeblement of the light by selection, and this practically precludes observation with standard candles. With gas-flames and glow-lamps the light is sufficient.

XVI. *On the Self-Regulation of the Compound Dynamo.* *By* A. W. RÜCKER, *M.A.*, *F.R.S.**

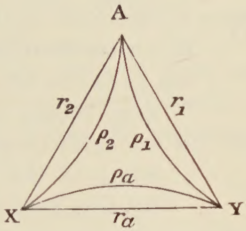
THE theory of the self-regulating power of the compound dynamo has not been treated in a satisfactory manner in any discussion of the subject with which I am acquainted. Some conclusions as to the proper method of constructing self-regulating dynamos have been drawn from equations in which the power of perfect self-regulation is assumed. As this perfection is known to be unattainable, no great weight can be given to arguments based on the assumption in question, and it will in the following paper be abandoned. A further inquiry will also be entered upon, viz. how far the conditions of good self-regulation are consistent with the other desiderata aimed at in the construction of a dynamo—such, for instance, as high efficiency.

The entire investigation will be based on Frölich's equation,

* Read April 25, 1885.

which expresses the electromotive force in terms of the current and the constants of the machine, and will therefore not apply in cases where the prejudicial effect of the magnetization of the armature is apparent. The notation and diagrammatic representation of the machine are those which I have found useful for teaching purposes.

Let the points A, X, Y be joined by three straight and three curved lines.



Let the side X Y represent the armature of the machine. The points A, X, and Y may be called its terminals. The curved lines represent the magnetizing coils of the inducing magnets; the straight lines A X and A Y represent external resistances.

Let the values of the resistances be as indicated in the figure. Let the total electromotive force be E, that between Y and A e_1, and that between A and X e_2. The currents in r_1 and ρ_1 may be represented by c_1 and γ_1, and a similar notation used for the other conductors.

Finally, let the whole resistance be R, let the resistances of the multiple arcs between Y A and A X be R'_1 and R'_2 respectively, and let c' be the total current in each of these multiple arcs.

The current is to be conceived as flowing out of the armature at Y, passing on to the three conductors ρ_a, ρ_1, and r_1, and returning at X.

All the existing forms of dynamo can be represented by leaving out some of the conductors shown in the above symmetrical figure. Their properties are perhaps more easily recognized by regarding them as particular cases of a more highly generalized machine. The notation used has also another advantage. The shunt in the Compound Dynamo may be used in one of two ways—viz. as a shunt upon the armature alone, or as a shunt upon the armature and series-coils. It is usual to represent its resistance by a symbol which indicates only that it is a shunt, without showing in which of these ways it is used. If, however, it is agreed that r_2 shall always represent the external resistance, r_1 being in any prac-

tical case infinite, then ρ_1 always represents the series-coils, and ρ_a or ρ_2 the shunt-coil according as it is applied in the first or second of the methods above referred to.

If we adopt Frölich's equation we may write

$$E = \frac{nM(s_0\gamma_0 + s_a\gamma_a + s_1\gamma_1 + s_2\gamma_2)}{1 + \sigma(s_0\gamma_0 + s_a\gamma_a + s_1\gamma_1 + s_2\gamma_2)};$$

where n represents the number of revolutions;

M is a constant depending on the machine;

s_a, s_1, and s_2 are the number of turns made by the magnetizing spirals ρ_a, ρ_1, and ρ_2;

and σ is a small constant depending on the gradual weakening of the magnetizing effects of the currents as the iron approaches saturation.

The product $s_0\gamma_0$ represents the number of ampere-turns by which the initial magnetic field is, or may be supposed to be, produced. If γ_0 is an independent current, this quantity may be large. If it is only a fictitious current which is regarded as the cause of the permanent magnetism, $s_0\gamma_0$ is small. If the product of $s_0\gamma_0$ and of σ may be neglected, and if $Ms_0\gamma_0 = k$, we may write

$$E = nk + \frac{nM(s_a\gamma_a + s_1\gamma_1 + s_2\gamma_2)}{1 + \sigma(s_a\gamma_a + s_1\gamma_1 + s_2\gamma_2)};$$

We have at once

$$\frac{\gamma_a}{\frac{1}{\rho_a}} = \frac{c'}{\frac{1}{R'_1 + R'_2}} = \frac{c_a}{\frac{1}{\rho_a} + \frac{1}{R'_1 + R'_2}},$$

$$\gamma_1\rho_1 = c'R'_1 \text{ and } \gamma_2\rho_2 = c'R'_2.$$

Hence

$$E - nk = \frac{nM\left\{s_a\frac{R'_1 + R'_2}{\rho_a} + s_1\frac{R'_1}{\rho_1} + s_2\frac{R'_2}{\rho_2}\right\}c'}{1 + \sigma\left\{s_a\frac{R'_1 + R'_2}{\rho_a} + s_1\frac{R'_1}{\rho_1} + s_2\frac{R'_2}{\rho_2}\right\}c'}.$$

But

$$c' = \frac{\rho_a c_a}{R'_1 + R'_2 + \rho_a} = \frac{\rho_a}{R'_1 + R'_2 + \rho_a} \times \frac{E}{R}.$$

Hence, if we write

$$\left\{s_a\frac{R'_1 + R'_2}{\rho_a} + s_1\frac{R'_1}{\rho_1} + s_2\frac{R'_2}{\rho_2}\right\}\frac{\rho_a}{R'_1 + R'_2 + \rho_a} = S,$$

we get
$$E-nk=\frac{nMSE}{R}\Big/\left(1+\frac{\sigma SE}{R}\right),$$
or
$$(E-nk)\left(E+\frac{R}{\sigma S}\right)=\frac{nM}{\sigma}E.$$

If the machine has no external excitement k may be neglected, unless the conditions under which it begins to work are under investigation. Hence the equation becomes
$$E=\{nM-R/S\}/\sigma. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If there is external excitement and the magnets have not reached the condition where the evidences of approaching saturation become important, terms in σ may be neglected, and we have
$$E=\frac{nkR/S}{R/S-nM}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

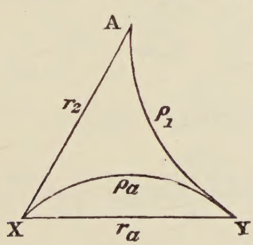
If k and σ be both neglected these equations lead to conclusions of no practical value; for if $nM=R/S$, both (1) and (2) make E indeterminate; and if $nM \neq R/S$, we get $E=\infty$ from (1) and $E=0$ from (2).

These results prove that no true approximation to the behaviour of the machine can be obtained by neglecting both the constants k and σ.

The above equations are exactly similar in form to those ordinarily given as applying to series and shunt machines; though, from the more general meaning assigned to the constants, they are in reality of a more general character.

Let us now apply them to the compound dynamo. Of the two forms of this machine, which, following the example of Prof. S. Thompson, we may call the Short-Shunt and the Long-Shunt respectively, we will take the former first.

Short-Shunt Compound Dynamo.



In this case $r_1=\rho_2=\infty$.

The conductors ρ_1 and ρ_a represent the series- and shunt-coils, and r_2 represents the external resistance.

Hence

$$R'_1=\rho_1, \quad R'_2=r_2,$$

$$R=r_a+\frac{\rho_a(r_2+\rho_1)}{r_2+\rho_1+\rho_a}=\frac{(r_2+\rho_1)(r_a+\rho_a)+r_a\rho_a}{r_2+\rho_1+\rho_a},$$

$$S=\left\{s_a\frac{r_2+\rho_1}{\rho_a}+s_1\right\}\frac{\rho_a}{r_2+\rho_1+\rho_a}.$$

Neglecting k, we get

$$E=\frac{1}{\sigma}\left\{nM-\frac{(r_2+\rho_1)(r_a+\rho_a)+r_a\rho_a}{s_a(r_2+\rho_1)+s_1\rho_a}\right\}.$$

Again, since

$$\frac{e_2}{c_2r_2}=\frac{E}{c_aR} \text{ and } \frac{c_2}{\frac{1}{r_2+\rho_1}}=\frac{\gamma_a}{\frac{1}{\rho_a}}=\frac{c_a}{\frac{r_2+\rho_1+\rho_a}{(r_2+\rho_1)\rho_a}},$$

$$E=e_2\frac{r_2+\rho_1+\rho_a}{\rho_a}\times\frac{R}{r_2}$$

$$=e_2\frac{(r_2+\rho_1)(r_a+\rho_a)+r_a\rho_a}{r_2\rho_a}.$$

Whence

$$e_2=\frac{1}{\sigma}\left\{\frac{nMr_2\rho_a}{r_2(r_a+\rho_a)+\rho_1(r_a+\rho_a)+r_a\rho_a}-\frac{r_2\rho_a}{r_2s_a+(s_a\rho_1+s_1\rho_a)}\right\},$$

which may be written

$$e_2=\frac{P_1}{A_1+x_1}-\frac{Q_1}{B_1+x_1},$$

if

$$P_1=\frac{nM\rho_a}{\sigma\{\rho_1(r_a+\rho_a)+r_a\rho_a\}}, \quad A_1=\frac{r_a+\rho_a}{\rho_1(r_a+\rho_a)+r_a\rho_a}, \quad \cdot \quad (3)$$

$$Q_1=\frac{\rho_a}{\sigma(s_a\rho_1+s_1\rho_a)}, \quad B_1=\frac{s_a}{s_a\rho_1+s_1\rho_a}, \quad x_1=\frac{1}{r_2}.$$

In like manner, since $c_2=e_2/r_2$,

$$c_2=\frac{1}{\sigma}\left\{\frac{nM\rho_a}{r_2(r_a+\rho_a)+\rho_1(r_a+\rho_a)+r_a\rho_a}-\frac{\rho_a}{r_2s_a+(s_a\rho_1+s_1\rho_a)}\right\},$$

which may be written

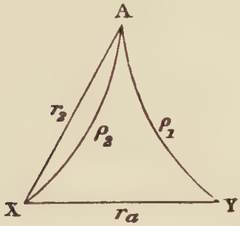
$$c_2=\frac{P_2}{A_2+x_2}-\frac{Q_2}{B_2+x_2},$$

if

$$P_2 = \frac{nM\rho_a}{\sigma(r_a+\rho_a)}, \quad A_2 = \frac{\rho_1(r_a+\rho_a)+r_a\rho_a}{r_a+\rho_a}, \qquad (4)$$

$$Q_2 = \frac{\rho_a}{\sigma s_a}, \quad B_2 = \frac{s_a\rho_1+s_1\rho_a}{s_a}, \quad x_2 = r_2.$$

Long-Shunt Compound Dynamo.



In this case $\qquad r_1 = \rho_a = \infty$.

The conductors ρ_1 and ρ_2 represent the series- and shunt-coils, and r_2 represents the external resistance.

Hence

$$R'_1 = \rho_1, \quad R'_2 = r_2\rho_2/(r_2+\rho_2),$$

$$R = r_a+\rho_1+\frac{r_2\rho_2}{r_2+\rho_2} = \frac{r_2(r_a+\rho_1+\rho_2)+\rho_2(r_a+\rho_1)}{r_2+\rho_2},$$

$$S = s_1+s_2\frac{r_2}{r_2+\rho_2} = \frac{r_2(s_1+s_2)+s_1\rho_2}{r_2+\rho_2};$$

whence we get

$$E = \frac{1}{\sigma}\left\{nM - \frac{r_2(r_a+\rho_1+\rho_2)+\rho_2(r_a+\rho_1)}{r_2(s_1+s_2)+s_1\rho_2}\right\}.$$

Also, since

$$\frac{e_2}{\dfrac{r_2\rho_2}{r_2+\rho_2}} = \frac{E}{R},$$

$$e_2 = \frac{1}{\sigma}\left\{\frac{nMr_2\rho_2}{r_2(r_a+\rho_1+\rho_2)+\rho_2(r_a+\rho_1)} - \frac{r_2\rho_2}{r_2(s_1+s_2)+s_1\rho_2}\right\};$$

which may be written

$$e_2 = \frac{P_3}{A_3+x_3} - \frac{Q_3}{B_3+x_3},$$

if

$$P_3 = \frac{nM}{\sigma(r\ \ +\rho_1)}, \quad A_3 = \frac{r_a+\rho_1+\rho_2}{\rho_2(r_a+\rho_1)}, \quad . \quad . \qquad (5)$$

$$Q_3 = \frac{1}{\sigma s_1}, \quad B_3 = \frac{s_1+s_2}{s_1\rho_2}, \quad x_3 = \frac{1}{r_2}.$$

And, as before,

$$c_2 = \frac{P_4}{A_4 + x_4} - \frac{Q_4}{B_4 + x_4},$$

if

$$P_4 = \frac{nM\rho_2}{\sigma(r_a + \rho_1 + \rho_2)}, \quad A_4 = \frac{\rho_2(r_a + \rho_1)}{r_a + \rho_1 + \rho_2}, \quad . \quad . \quad (6)$$

$$Q_4 = \frac{\rho_2}{\sigma(s_1 + s_2)}, \quad B_4 = \frac{s_1\rho_2}{s_1 + s_2}, \quad x_4 = r_2.$$

We thus see that if the current or difference of potential which it is required to maintain as constant as possible be represented by the general symbol ϕ, then, in the case of either machine,

$$\phi = P / (A + x) - Q / (B + x);$$

where A, B, P, and Q do not depend upon the variable resistance, and where x is either the resistance or the conductivity of the variable conductor.

All problems on self-regulation in the case of either machine may therefore be solved by means of this formula, and the application of the results is made by giving to the constants the values proper to the machine, and to the meaning of the symbol ϕ in the particular case under consideration.

It will be observed that the constant A is always either the resistance, or the reciprocal of the resistance offered by the machine to a current produced by a battery placed in the external circuit—*i. e.* it is either the resistance or the conductivity of the machine. If that resistance be represented by R_m, $A = R_m$ if ϕ is the external current, and $A = 1 / R_m$ if it is the external electromotive force.

If μ and m are respectively the largest and smallest values of x between which self-regulation is aimed at, then $\mu - m$ may be called the *range* of x. There will in general be some particular value of x which will be most frequently employed. This may be called the *usual value* of x, and may be denoted by ξ. As it is sometimes necessary to distinguish between the cases in which x is a resistance and a conductivity, the value of r_2 which corresponds to ξ will be indicated by $\bar{r}_2$.

Conditions of Efficiency.

Although a self-regulating machine is primarily intended to supply the same current or electromotive force whatever

(within certain limits) the resistance of the external circuit may be, it is nevertheless desirable that it should be as efficient as possible. It is well known that the efficiency is a maximum for a given value of the external resistance; and it is evident that the machine should not only have a high efficiency, but that the maximum should, if possible, be attained under the ordinary conditions of working.

1. *Short-Shunt Machine.*

Let η be the electrical efficiency. Then

$$\eta = \frac{e_2^2}{r_2} \Big/ \frac{E^2}{R} = \frac{\rho_a^2}{(r_2+\rho_1+\rho_a)^2} \times \frac{r_2}{R}$$

$$= \frac{\rho_a^2}{r_2+\rho_1+\rho_a} \times \frac{r_2}{(r_2+\rho_1)(r_a+\rho_a)+r_a\rho_a}.$$

Taking the logarithms of both sides and differentiating with respect to r_2, we get

$$\frac{1}{\eta}\frac{d\eta}{dr_2} = \frac{1}{r_2} - \frac{1}{r_2+\rho_1+\rho_a} - \frac{r_a+\rho_a}{(r_2+\rho_1)(r_a+\rho_a)+r_a\rho_a},$$

which vanishes if

$$r_2^2(r_a+\rho_a) = (\rho_1+\rho_a)\{\rho_1(r_a+\rho_a)+r_a\rho_a\}. \quad . \quad . \quad . \quad (7)$$

Let r'_2 be the positive root of this equation. Hence, since

$$(r'_2+\rho_1)(r_a+\rho_a)+r_a\rho_a = (r'_2+\rho_1)\rho_a + r_a\{r'_2+\rho_1+\rho_a\},$$

and from (7),

$$r_a\{r'^2_2-(\rho_1+\rho_a)^2\} = \rho_a\{\rho_1(\rho_1+\rho_a)-r'^2_2\},$$

or

$$r_a\{r'_2+\rho_1+\rho_a\} = \rho_a\frac{\rho_1(\rho_1+\rho_a)-r'^2_2}{r'_2-(\rho_1+\rho_a)},$$

we have

$$(r'_2+\rho_1)(r_a+\rho_a)+r_a\rho_a$$
$$= \rho_a\left\{r'_2+\rho_1+\frac{\rho_1(\rho_1+\rho_a)-r'^2_2}{r'_2-(\rho_1+\rho_a)}\right\}$$
$$= -\frac{r'_2\rho_a^2}{r'_2-(\rho_1+\rho_a)}.$$

Substituting this in the expression for η, we get

$$\eta = \frac{\rho_1+\rho_a-r'_2}{\rho_1+\rho_a+r'_2}, \text{ or } \rho_1+\rho_a = r'_2(1+\eta)/(1-\eta).$$

Hence, from (7),

$$\frac{r_a+\rho_a}{\rho_1(r_a+\rho_a)+r_a\rho_a}=\frac{1+\eta}{1-\eta}\times\frac{1}{r'_2};$$

and from (3) and (4),

$$A_1=\frac{1+\eta}{1-\eta}\xi \text{ and } A_2=\frac{1-\eta}{1+\eta}\xi, \quad . \quad . \quad . \quad . \quad (8)$$

if we suppose r'_2 to be $=\bar{r}_2$, *i. e.* if the machine is so designed that the usual value of the external resistance is that which gives the maximum efficiency.

2. *Long-Shunt Machine.*

In this case

$$\eta=\frac{e_2^2}{r_2}\Big/\frac{E^2}{R}=\frac{\rho_2^2}{(r_2+\rho_2)^2}\times\frac{r_2}{R}$$

$$=\frac{\rho_2^2}{r_2+\rho_2}\times\frac{r_2}{r_2(r_a+\rho_1+\rho_2)+\rho_2(r_a+\rho_1)};$$

and, as before, $d\eta/dr_2=0$ if

$$\frac{1}{r'_2}-\frac{1}{r'_2+\rho_2}-\frac{r_a+\rho_1+\rho_2}{r'_2(r_a+\rho_1+\rho_2)+\rho_2(r_a+\rho_1)}=0;$$

$$\therefore \quad r'^2_2(r_a+\rho_1+\rho_2)=\rho_2^2(r_a+\rho_1), \quad . \quad . \quad . \quad . \quad (9)$$

or

$$r_a(\rho_2^2-r'^2_2)=r'^2_2(\rho_1+\rho_2)-\rho_1\rho_2^2.$$

Hence

$$r_a(r'_2+\rho_2)+r'_2(\rho_1+\rho_2)+\rho_1\rho_2$$

$$=\frac{r'^2_2(\rho_1+\rho_2)-\rho_1\rho_2^2}{\rho_2-r'_2}+r'_2(\rho_1+\rho_2)+\rho_1\rho_2$$

$$=\frac{r'_2\rho_2^2}{\rho_2-r'_2}.$$

Substituting in the expression for η, we obtain

$$\eta=\frac{\rho_2-r'_2}{\rho_2+r'_2}, \text{ or } \rho_2=r'_2(1+\eta)/(1-\eta).$$

Hence, from (5), (6), and (9), if, as before, $r'_2=\bar{r}_2$,

$$\left.\begin{aligned}A_3&=\frac{1+\eta}{1-\eta}\times\frac{1}{\bar{r}_2}=\frac{1+\eta}{1-\eta}\xi,\\ A_4&=\frac{1-\eta}{1+\eta}\times\bar{r}_2=\frac{1-\eta}{1+\eta}\xi.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

The above values for A will be required hereafter; but if we replace A by its value in terms of R_m, equations (8) and

(10) may all be summed up in the formula

$$(1-\eta)/(1+\eta)=R_m/r'_2,$$

or

$$\eta=(r'_2-R_m)/(r'_2+R_m).$$

In the case of the Short-Shunt Machine,

$$r'^2_2=(\rho_1+\rho_a)R_m \text{ from equation (7).}$$

$$\therefore \quad \eta=(\sqrt{\rho_1+\rho_a}-\sqrt{R_m})/(\sqrt{\rho_1+\rho_a}+\sqrt{R_m}).$$

In the case of the Long-Shunt Machine,

$$r'^2_2=\rho_2 R_m, \text{ from equation (9).}$$

$$\therefore \quad \eta=(\sqrt{\rho_2}-\sqrt{R_m})/(\sqrt{\rho_2}+\sqrt{R_m}).$$

These formulæ may be put in another form, which is useful as it is very easy to remember. In either kind of compound machine, and in the ordinary shunt dynamo, if the resistance of the armature is infinite, it is possible for a current generated in the external circuit to pass from one extremity of the external circuit to the other, *i. e.* from one terminal to the other, exclusively through wires which form parts of the magnetizing spirals. In the case of the Short-Shunt Machine this path includes both spirals; in the ordinary Shunt or in the Long-Shunt Compound Machine it includes one spiral only. If we call the resistance of this path Σ, then in all three cases the maximum efficiency is given by the equation

$$\eta=(\sqrt{\Sigma}-\sqrt{R_m})/(\sqrt{\Sigma}+\sqrt{R_m});$$

and the value of the external resistance for which the maximum efficiency is attained by

$$r'^2_2=\Sigma R_m.$$

In cases where the resistance of the shunt is large, approximate expressions may be deduced from the above by substituting the resistance of the shunt for Σ, and the sum of the resistances of the armature and series-coil for R_m.

If the maximum efficiency is attained when r_2 has its usual value, we may put the last expression in a form which will be useful hereafter. Let Y be a quantity which has with regard to Σ the same meaning as x with regard to r_2; *i. e.* let it be $=\Sigma$ or $1/\Sigma$ according as ϕ represents the external current or external electromotive force. Then

$$\eta=(\sqrt{Y}\sim\sqrt{A})/(\sqrt{Y}+\sqrt{A});$$

and if the maximum efficiency is attained for the usual value of x,

$$\xi^2=\mathrm{YA}.$$

Conditions of Maximum Power.

Since the power of a dynamo is expressed by either of the formulæ e_2^2/r_2 or $c_2^2 r_2$, it is in all cases given by $\phi^2 x$.

This has a critical value if

$$2x\frac{d\phi}{dx}+\phi=0\,;$$

i. e. if

$$2x\left\{-\frac{\mathrm{P}}{(\mathrm{A}+x)^2}+\frac{\mathrm{Q}}{(\mathrm{B}+x)^2}\right\}+\frac{\mathrm{P}}{\mathrm{A}+x}-\frac{\mathrm{Q}}{\mathrm{B}+x}=0\,;$$

i. e. if

$$\frac{\mathrm{P}(\mathrm{A}-x)}{(\mathrm{A}+x)^2}+\frac{\mathrm{Q}(\mathrm{B}-x)}{(\mathrm{B}+x)^2}=0.$$

Conditions of Self-Regulation.

Since

$$\phi=\frac{\mathrm{P}}{\mathrm{A}+x}-\frac{\mathrm{Q}}{\mathrm{B}+x},$$

$$\therefore\ \frac{d\phi}{dx}=-\frac{\mathrm{P}}{(\mathrm{A}+x)^2}+\frac{\mathrm{Q}}{(\mathrm{B}+x)^2}.$$

Hence ϕ has two critical values corresponding to the values of x given by the equation

$$x(\sqrt{\mathrm{P}}\mp\sqrt{\mathrm{Q}})=-\mathrm{B}\sqrt{\mathrm{P}}\pm\mathrm{A}\sqrt{\mathrm{Q}}.$$

If we take the lower signs, x is necessarily negative unless B is negative; which can only be the case if some of the inducing spirals are wound in the negative direction, *i. e.* so that they reduce the strength of the magnetic field. If B is negative, it is evident that ϕ is infinite for a positive value of x. This unintelligible result is explained by reference to the general equation in which both k and σ are included, viz.

$$(\mathrm{E}-nk)(\mathrm{E}+\mathrm{R}/\sigma\mathrm{S})=n\mathrm{ME}/\sigma.$$

For if some of the quantities s_a, s_1, or s_2 are negative, and if the value of r_2 is such that $\mathrm{S}=0$, then $\mathrm{E}=nk$. The approximate expression which is being discussed fails therefore in this case, but it applies to cases in which one of the spirals is wound in the negative direction but in which B remains

positive. Reference to the expressions for B shows that this will be the case in the Short-Shunt Machine if the series-coils are negative and if the number of turns is $< s_a \rho_1 / \rho_a$, and in the Long-Shunt Machine if the shunt-coils are negative and if $s_2 < s_1$. In other cases Q is negative also.

Confining our attention therefore to the case in which B is positive, let X be the critical value of x, and Φ the corresponding value of ϕ.

Then

$$X = (A\sqrt{Q} - B\sqrt{P}) / (\sqrt{P} - \sqrt{Q}), \quad . \quad . \quad (11)$$

$$\Phi = (\sqrt{P} - \sqrt{Q})^2 / (A - B). \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Also

$$\frac{d^2\phi}{dx^2} = \frac{2P}{(A+x)^3} - \frac{2Q}{(B+x)^3};$$

whence, at the critical point,

$$\frac{d^2\phi}{dx^2} = -2(\sqrt{P} - \sqrt{Q})^4 / (A-B)^3 \sqrt{PQ}. \quad . \quad . \quad (13)$$

Hence if $A > B$, Φ is positive and is a maximum; and if $A < B$, Φ is negative and is a minimum.

The value of X given by (11) is not necessarily positive, and hence we must consider a number of cases which differ from each other in the relative magnitudes of A, B, P, and Q. In distinguishing between them, it is convenient to remember that

$$\phi = \frac{x(P-Q) + BP - AQ}{(A+x)(B+x)}.$$

It follows from this expression and from (11) that

(I.) If $P/Q < A/B < 1$,

ϕ is negative for all positive values of x.

(II.) If $A/B < P/Q < 1$,

ϕ is positive for values of $x < (BP - AQ)/(Q - P)$.

(III.) If $A/B < 1 < \sqrt{P}/\sqrt{Q}$, and therefore $< P/Q$,

ϕ is positive for all positive values of x.

In both these last cases ϕ has no maximum value; for in (II.) X is positive but $> (BP - AQ)/(Q - P)$, while in (III.) it is negative.

Next, taking cases in which $A-B$ is positive, we see that

(IV.) If $A/B>1>P/Q$,

ϕ is negative for all positive values of x.

(V.) If $A/B>P/Q>1$,

ϕ is positive for values of $x>(AQ-BP)/(P-Q)$.

(VI.) If $P/Q>A/B>\sqrt{P}/\sqrt{Q}>1$,

ϕ is positive for all positive values of x.

In cases (V.) and (VI.) ϕ has a maximum value corresponding to a positive value of x.

(VII.) If $\sqrt{P}/\sqrt{Q}>A/B>1$,

ϕ is positive for all positive values of x, and X is negative, so that there is no maximum value of ϕ.

The physical meaning of these different conditions may be best understood by considering the inequalities

$$P/Q> \text{ or } <1 \text{ and } P/Q> \text{ or } <A/B.$$

If ϕ represents the external electromotive force, the first of these becomes, in the case of the Short-Shunt and Long-Shunt Machines respectively,

$$nM(s_a\rho_1+s_1\rho_a)> \text{ or } <\rho_1r_a+\rho_1\rho_a+r_a\rho_a, \quad . \quad . \quad (14)$$

and

$$nMs_1> \text{ or } <r_a+\rho_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

But, by equation (1), the condition that the velocity is greater or less than the critical speed is

$$nM> \text{ or } <R/S;$$

and if, in the case of the Short-Shunt Machine, we put $r_2=0$, this becomes for the values of R and S given above,

$$nM> \text{ or } <\frac{\rho_1r_a+\rho_1\rho_a+r_a\rho_a}{s_a\rho_1+s_1\rho_a},$$

which is identical with (14).

Similarly, in the case of the Long-Shunt Machine, we get for the same condition,

$$nM> \text{ or } <\frac{r_a+\rho_1}{s_1},$$

which is identical with (15).

Hence, in these cases,

$$P/Q> \text{ or } <1$$

according as the speed is greater or less than the critical speed for the resistance of the circuit when the external resistance is zero.

In like manner, it can be shown that if ϕ represents the external current, the expression $P/Q >$ or < 1 according as the speed is greater or less than the critical speed when the external resistance is infinite.

Inasmuch, however, as $x=1/r_2$ when ϕ is the external electromotive force, and $x=r_2$ when ϕ is the external current, these results may be briefly expressed by saying that P/Q is $>$ or <1, according as the speed is greater or less than the critical speed when x is infinite.

Similarly it may be proved that

$P/Q >$ or $< A/B$ according as the speed is greater or less than the critical speed when x vanishes.

On referring to the conditions laid down in the seven cases distinguished above in the light of these explanations, we see that they may be readily interpreted. The constant P is proportional to the speed, and we may conceive the ratio P/Q to be gradually increased by augmenting the velocity of revolution.

Thus when $A-B$ is positive, Case IV. is that in which the velocity is less than the critical velocities when $x=0$ or ∞.

In Case V. the velocity is greater than the critical velocity when $x=\infty$, and less than that when $x=0$.

In Cases VI. and VII. it is greater than either of these critical velocities.

The condition that there shall be a maximum value of ϕ is

$$A/B > \sqrt{P}/\sqrt{Q} > 1.$$

As an example of how such general formulæ can be applied to a particular case, we deduce from this relation and from equations (3) that, in the case of the Short-Shunt Dynamo, the external electromotive force can only have a maximum value if

$$\frac{r_a+\rho_a}{\rho_1(r_a+\rho_a)+r_a\rho_a}\cdot\frac{s_a\rho_1+s_1\rho^a}{s_a} > \sqrt{\left(\frac{nM(s_a\rho_1+s_1\rho_a)}{\rho_1(r_a+\rho_a)+r_a\rho_a}\right)} > 1\,;$$

or if

$$\frac{\rho_1+\frac{s_1}{s_a}\rho_a}{\rho_1+\frac{r_a}{r_a+\rho_a}\cdot\rho_a} > \frac{nMs_a}{r_a+\rho_a} > \frac{\rho_1+\frac{r_a}{r_a+\rho_a}\cdot\rho_a}{\rho_1+\frac{s_1}{s_a}\rho_a}\,;$$

whence it follows that we must have

$$\frac{s_1}{s_a} > \frac{r_a}{r_a+\rho_a}.$$

Similar deductions can be made in the other cases.

The fact that if P / Q be sufficiently large there is no maximum value of ϕ for any positive value of x, means that if the velocity is so great that the inducing magnets are saturated so that the total electromotive force is constant, any increase in the resistance of the external circuit must be accompanied by a decrease in the current which flows through it and an increase in the electromotive force at its extremities. In the former case $x=r_2$, and in the latter $x=1/r_2$, so that in both cases an increase in x produces a decrease in ϕ. This state of things is reached before complete saturation, viz. at the point when the prejudicial effect due to the weakening of the current produced by an increase in r_2 overbalances the advantage gained by the fact that a larger proportion of the whole current passes through the shunt. This point is reached when

$$\sqrt{P}/\sqrt{Q}=A/B.$$

We are now in a position to discuss the amount of change in ϕ produced by a given finite change in x, i. e. the self-regulating power of the dynamo.

The treatment of this question must be slightly varied, according as a maximum value of ϕ does or does not occur for a value of x intermediate to μ and m, the largest and smallest values of that quantity between which self-regulation is aimed at.

If it does not, we may write

$$\left.\begin{aligned}\frac{P}{A+m}-\frac{Q}{B+m}&=\phi_1,\\ \frac{P}{A+\mu}-\frac{Q}{B+\mu}&=\frac{\phi_1}{1+q},\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (16)$$

where ϕ_1 is the value of the electromotive force or current to be kept constant, and q is a quantity which will be smaller as the self-regulation is more perfect, and which will be positive or negative according as ϕ diminishes or increases as x increase.

If, on the other hand, X lies between μ and m, then the

equations corresponding to (16) become

$$\left.\begin{aligned}\frac{P}{A+m}-\frac{Q}{B+m}&=\frac{\Phi}{1+p'},\\ \frac{P}{A+\mu}-\frac{Q}{B+\mu}&=\frac{\Phi}{1+p''},\end{aligned}\right\} \quad . \quad . \quad . \quad (17)$$

where Φ is the maximum value of ϕ.

If the constants are so chosen that the values of ϕ corresponding to μ and m are equal, then

$$\frac{P}{A+m}-\frac{Q}{B+m}=\frac{P}{A+\mu}-\frac{Q}{B+\mu}=\frac{\Phi}{1+p}, \quad . \quad . \quad (18)$$

where Φ is the maximum value of ϕ.

If, now, the following quantities are given, viz. :—

(1) the value of ϕ which is to be attained (ϕ_1 or Φ);

(2) the extreme values of x (μ and m);

(3) the percentage variation in the value of ϕ which can be allowed ($100q$ or $100p$);

(4) the usual value of x (ξ), together with the condition that the maximum efficiency shall be attained for that value;

(5) the value of the required maximum efficiency;

then we have four equations, viz. *either* (16) or (17) and the two equations which connect η and ξ with A and Y (see p. 104) to be satisfied by the five constants A, Y, B, P, and Q. Of these, A and Y are absolutely determined by the conditions; but any one of the three P, Q, or B may be given any convenient value if the maximum value of Φ does not lie between μ and m. If it does, we have the additional relation

$$\Phi=(\sqrt{P}-\sqrt{Q})^2/(A-B);$$

and if the values of both p' and p'' are assigned, there are in all five equations by which the five constants are determined. When these five quantities are known, we may equate them to their appropriate values in terms of the resistances &c. of the various parts of the machine; and we thus obtain five equations between eight quantities, viz.:—n, M, σ, s_1, s_a (or s_2), r_a, ρ_1, ρ_a (or ρ_2); in the selection of which, therefore, there is considerable range for choice.

Although the problem of the Self-Regulation of the Compound Dynamo is solved as far as the algebra is concerned,

it is possible that the values of P, Q, &c. found for arbitrarily selected values of ϕ, μ, m, &c. may be negative, or such as it would be impossible to attain in practice.

The question as to what value of q it is physically possible to attain in any given case can only be answered if we have regard to the limitations to the values of A, B, P, and Q which apply to that case. If this be done, it is possible to obtain limits to q, that is to the perfection of self-regulation.

I shall add two examples of the use of equations (16) and (18) for this purpose.

Case III. $A<B$, $P>Q$.

As the values of ϕ diminish as x increases, the value which corresponds to μ must be less than that which correspond to m. Hence

$$\frac{P}{A+m}-\frac{Q}{B+m}=\phi_1,$$

$$\frac{P}{A+\mu}-\frac{Q}{B+\mu}=\frac{\phi_1}{1+q}.$$

Solving for P and Q, we get

$$P=\frac{\phi_1}{1+q}\cdot\frac{\mu-m-q(B+m)}{(A-B)(\mu-m)}(A+\mu)(A+m),$$

$$Q=\frac{\phi_1}{1+q}\cdot\frac{\mu-m-q(A+m)}{(A-B)(\mu-m)}(B+\mu)(B+m).$$

Now since $A-B$ is negative, we must, if P and Q are positive, have

$$q>(\mu-m)/(A+m),$$

and, *a fortiori*,

$$>(\mu-m)/(B+m).$$

Further, since $P>Q$,

$$\{q(B+m)-(\mu-m)\}(A+\mu)(A+m)>$$
$$\{q(A+m)-(\mu-m)\}(B+\mu)(B+m);$$

$$\therefore\ q(A+m)(B+m)(B-A)<(\mu-m)\{B^2-A^2$$
$$+(\mu+m)(B-A)\};$$

$$\therefore\ q(A+m)(B+m)<(\mu-m)\{A+B+\mu+m\}.$$

Cases V. *and* VI.—$A/B > \surd P/\surd Q > 1$.

Taking next the case in which the values of ϕ corresponding to μ and m are equal, we deduce from (18)

$$P = \frac{\Phi}{1+p}\frac{(A+\mu)(A+m)}{A-B},$$

$$Q = \frac{\Phi}{1+p}\frac{(B+\mu)(B+m)}{A-B}.$$

Substituting these values in the equation

$$\Phi = (\surd P - \surd Q)^2/(A-B),$$

we get

$$(A-B)^2(1+p) = \{\sqrt{(A+\mu)(A+m)} - \sqrt{(B+\mu)(B+m)}\}^3;$$

which reduces to

$$\{(A-B)p+\mu-m\}^2 = 4p(A+m)(B+\mu).$$

Solving for B, we get

$$Bp = Ap+\mu+m+2A \pm 2\sqrt{(A+\mu)(A+m)(1+p)}.$$

Hence, since $A > B$, Ap must be greater than the right-hand side of the equation. This inequality can only hold if we take the negative sign, and if

$$2\sqrt{(A+\mu)(A+m)(1+p)} > (A+\mu)+(A+m),$$

i. e. if

$$4p(A+\mu)(A+m) > (\mu-m)^2;$$

whence

$$p > \frac{(\mu-m)^2}{4(A+\mu)(A+m)}.$$

Also, since B is positive,

$$Ap+(A+\mu)+(A+m) > 2\sqrt{(A+\mu)(A+m)(1+p)};$$

$$\therefore\ 1+p-2\sqrt{1+p}\sqrt{(A+\mu)(A+m)}/A$$
$$+(A+\mu)(A+m)/A^2 > \mu m/A^2;$$

$$\therefore\ \{\sqrt{1+p}-\sqrt{(A+\mu)(A+m)}/A\}^2 > \mu m/A^2.$$

We find, therefore, that in both these cases an inferior limit can be found to p or q, which depends only on μ, m, and A. If, therefore, the latter quantity is determined by considerations relative to the efficiency, we implicitly determine at the same time a limit to the perfection of the self-regulation.

The last case is probably important practically, and the expression obtained shows that the inferior limit to p varies, if A is large, nearly as the square of the range. It will be less as A is greater; and this statement holds good for all the other cases enumerated above, so that a large value of A is favourable to good self-regulation. On referring to equations (8) and (10), we see that for a given usual value of x a high maximum efficiency is favourable to a large value of A if ϕ is the external electromotive force, and to a small value of A if ϕ is the external current. Hence we conclude that it is more difficult to combine a high efficiency with an approximately constant external current than with an approximately constant external electromotive force.

Postscript, April 30, 1885.

Since the above paper was read before the Physical Society, I have seen a solution of the question with which it deals, published by Dr. Frölich in the current number of the *Elektrotechnische Zeitschrift*, April 1885. I should like, therefore, to add a few words as to the relations between our investigations in respect both of time and result.

The method and chief conclusions given in my own paper, including the formulæ for ϕ, q, and the method of finding limits to the perfection of the regulation, were given to my Senior Class in Technical Electricity in February last. In March I had several engagements which made special calls upon my time, and partly on this account, partly because I wished to add a discussion of the case when Q or B is negative, I did not publish my results at once.

Towards the latter end of March I received my copy of the *Elektrotechnische Zeitschrift* for that month, which contained the first part of Dr. Frölich's paper. In that he gave the formulæ for the electromotive force, current, &c. in the cases of the series, shunt, and both forms of compound dynamo, in terms of the external and other resistances. The formulæ were not reduced to any simple form like the equation in ϕ given by me; and though the paper showed that Dr. Frölich was engaged on the question of self-regulation, it did not afford any indication of his method of attacking the problem. The next day after seeing this paper I sent my own investi-

gation to the Secretary of the Physical Society. It was brought before the Council of the Society on March 28th; but as it was thought that the matter was of some interest, the reading of the paper was postponed till the first Meeting after the Easter vacation (April 25th), and I was asked to attend for the purpose of giving an account of it myself. In the interval I made some improvements in the statements as to the physical meanings of the inequalities which I described at the Meeting, and have incorporated these in the text. It is only since the paper was read that I have received the April number of the *Elektrotechnische Zeitschrift*, from which I learn that Dr. Frölich has "seit dem Abdrucke des ersten Theiles dieses Vortrages," and guided partly by theory, partly by experiment, arrived at a very satisfactory solution of the problem of obtaining a constant external electromotive force.

As far, therefore, as our work is common, I do not wish to question Dr. Frölich's undoubted right to claim prior publication. The above statement is, however, necessary to show that my results were obtained independently.

On comparing the two papers, it will be seen that I have throughout considered the problem with reference to the efficiency as well as to the self-regulation, and have given the equations a more general form, in which they apply, when the symbols are properly interpreted, either to the external electromotive force or to the external current. Dr. Frölich has dealt chiefly with the case of a constant electromotive force, in which the conditions of high efficiency and good self-regulation are in accord, and both can be sécured together. To obtain the best result, if a constant current is required, will need a careful balancing of opposing requirements.

As regards, however, the practical determination of another condition which shall render the problem determinate when a maximum value of ϕ does not occur between μ and m, Dr. Frölich has advanced the question a step beyond where I left it, and has added very greatly to the interest of his paper.

He has shown that when the external electromotive force is in question, and without any reference to the value of the external resistance for which the maximum efficiency occurs, excellent results may be obtained by taking (in the above

notation) $A^2Q=B^2P$. I had previously shown the physical meaning of this condition; geometrically it amounts to choosing the arbitrary constant, so that $d\phi / dx=0$ when $x=0$. Since, in the case under discussion, $x=1 / r_2$, Dr. Frölich's curves and mine are so related that the product of the abscissæ of corresponding ordinates is unity, and the tangent to my curve at the point where it meets the axis of ϕ becomes in Dr. Frölich's figures an asymptote.

As expressed by the curve between e_2 and r_2 (Dr. Frölich's), good self-regulation can only be obtained in this case for values of r_2 greater than that at which the curve may be considered to have become practically parallel to its asymptote. As expressed by the curve between e_2 and $1 / r_2$ (my own), the corresponding condition is that μ shall be small enough for the curve to be at the corresponding point practically parallel to the tangent at the point for which $x=0$. Dr. Frölich has shown that these conditions are fulfilled in practice, and has thus added very materially to the importance of his paper.

It must, however, be noted that this solution has nothing absolute about it unless the efficiency is considered. If it is left out of account another constant (A) is indeterminate, and may be chosen so as to make q a minimum. For when $A^2Q=B^2P$,

$$q=\frac{\mu-m}{(A+m)(B+m)} \times \frac{AB(\mu+m)+\mu m(A+B)}{AB+\mu(A+B)}.$$

In the case under consideration we may put $m=0$, and thus write

$$q=\mu^2 / \{AB+\mu(A+B)\};$$

which shows that, among the various solutions which satisfy the condition $A^2Q=B^2P$, that will give the best self-regulation for which A and B are largest.

The condition that A shall be large implies (since $A=1/R_m$) that the resistance of the machine must be small, the necessity for which could of course be readily foreseen. The condition that B should be large leads to less obvious conclusions. Thus, in the case of the Long-Shunt Machine,

$$B_3=(s_1+s_2) / s_1\rho_2;$$

and to make this as large as possible, we should have s_2/s_1

large and ρ_2 small. The first of these conditions is always, the second is never, fulfilled in practice. The reason of this is obvious, viz. that the efficiency would be reduced by diminishing the resistance of the shunt. The maximum efficiency is given by the formula

$$\eta = (\sqrt{\rho_2} - \sqrt{R_m}) / (\sqrt{\rho_2} + \sqrt{R_m}),$$

which diminishes with ρ_2. It is interesting therefore to note that a high shunt-resistance is not in itself conducive to good self-regulation; and that, within the bounds of Dr. Frölich's condition, there are still opportunities for choice by which improvements in the efficiency and regulation may be effected. Probably in practice the last adjustments will be best made by some system of experiment like that described by Dr. Frölich. The theory given above will, however, enable much to be done by a few preliminary calculations.

Since I read the paper, Prof. Silvanus Thompson has called my attention to the question as to whether my formulæ indicate the advantage of back winding in the case when a constant external current is desired. Dr. Frölich has constructed a machine on this principle, to which he was led by theory. To discuss this question fully would require an investigation of the problem when B is negative; but it may be remarked that in a case such as that discussed above, when a large value of B is desirable, it may be increased in the case of the Long-Shunt Machine (B_4) by taking s_2 negative and $< s_1$.

XVII. *On the Determination of the Heat-Capacity of a Thermometer.* By J. W. Clark, *Assistant Professor of Physics in University College, Liverpool**.

I. In the determination of specific heats a correction should be made for that part of the thermometer which is immersed in the water of the calorimeter, as its specific heat is not the same as that of an equal volume of water. Very often this correction is reduced to a mere estimation on

* Read April 25, 1885.

account of the unknown weights of glass and mercury which constitute the immersed portion of the thermometer.

When two metals of known specific gravity are fused together, and the volume of the resulting alloy is the sum of the volumes of its two constituents, it is only necessary to know the specific gravity and volume of the piece of alloy to calculate the exact volumes of the metals comprising it. Similarly, by determining the specific gravity and volume of the thermometer, the volume of mercury which it contains can be at once determined from

$$V_1 = \frac{V(S-S_2)}{S_1-S_2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where V_1 is the required volume of mercury in the thermometer,
V the volume of the thermometer,
S the specific gravity of the thermometer,
S_2 „ „ „ thermometer-glass,
S_1 „ „ of Hg.

The mean value of several very closely agreeing determinations of the specific gravity of different specimens of thermometer-glass is 3·199 for lead-glass and 2·512 for soda-glass. Should it not be known of which sort of glass the thermometer consists, it may be readily ascertained by slowly introducing the upper extremity of the instrument into the reducing-flame of a blowpipe:—Soda-glass yields a yellow flame, but lead-glass blackens, from the reduction of the oxide of lead which it contains. It may be assumed that thermometers made on the continent consist of soda-glass; those made in England are usually constructed of lead-glass.

The total volume of the thermometer (V) is obtained from its weight in air and in water.

The volume of mercury contained in the thermometer having been found by (1), the volume of that part of the thermometer which is immersed in the water of the calorimeter has next to be determined. This latter volume, less the contained volume of mercury, is the immersed volume of glass.

The total immersed volume (V_3) of the thermometer is best found from the weight (W) of the thermometer in air, and its weight (W_1) when dipped in water to the same depth as it

dipped into the water of the calorimeter ; then

$$V_3 = W^{\text{grm.}} - W_1^{\text{grm.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But, if the bulb be cylindrical and of the same diameter as the stem, this volume may be calculated from the measured length and diameter of the immersed portion; for if of an irregular shape it may be found by plunging it into a burette graduated in cubic centimetres and partly filled with water; but in both cases with a less satisfactory result than is given by (2).

The volume of the *glass* of the thermometer (V_2) immersed in the water of the calorimeter is then

$$V_2 = V_3 - V_1.$$

These volumes of glass and mercury are converted into their corresponding weights, using the mean specific gravities of lead- and soda-glass already given. The sum of the products of the weight of the immersed glass and its specific heat, and of the weight of the mercury and its specific heat, is the required water-value of the part of the thermometer dipping into the water in the calorimeter.

Regnault has given the specific heat of thermometer-glass as 0·2; but for greater accuracy it would be desirable that for this value the mean specific heat of lead or of soda thermometer-glass should be substituted according to circumstances *.

The following is an illustration of the application of the method :—

Thermometer No. 2. Soda-glass.

Weight of thermometer in air . . .	$=W$	33·97 grm.
" " water . .		23·01 grm.
Volume of thermometer . . .	$=V$	10·96 c. c.
Specific gravity of thermometer . .	$=S$	3·098
Mean sp. gr. of soda-glass	$=S_2$	2·512
Sp. gr. of Hg	$=S_1$	13·6

Volume of mercury in thermometer $= V_1 = \dfrac{V(S-S_2)}{S_1-S_2}$ $=0·5795$ c.c.

* It may perhaps be serviceable to call attention to the *Physikalisch-Chemische Tabellen* of Landolt and Börnstein as a work which contains a most useful collection of data.

Weight of thermometer in air	33·97 grm.
Weight of thermometer with lower end immersed in water to the same depth as it was immersed in water of calorimeter	29·73
Loss of weight = volume of immersed part of thermometer	4·24 c.c.
Subtract contained volume of $Hg = V_1$.	= 0·5797
to get immersed volume of thermometer-glass	= 3·661 c.c.
Weight of this volume of thermometer-glass $3·661 \times 2·512$ . . . . =	9·196 grm.
Weight of contained Hg $0·5795 \times 13·6$.	= 7·881
Water-value of immersed glass $9·324 \times 0·2$	= 1·840
Water-value of immersed Hg $7·881 \times 0·0335$	= 0·2639
Total water-value of the immersed part of the thermometer	2·1039

To test the reliability of the method, I sacrificed the thermometer by cutting off the stem at the level at which it was immersed in the water of the calorimeter, and weighed the quantities of glass and mercury: there were 9·63 and 7·64 grms. respectively, corresponding to a water-value of 2·182, *which ascribes to the above method an error of* 3·7 *per cent. in the required correction.* This negligible error is due to the volume of the thermometer—consisting, not only of glass and mercury, but also of the unfilled bore of the tube—and to slight deviation of the specific gravity of the thermometer-glass from the mean specific gravity used in the calculation. It may be just worth pointing out that when a fragment of the thermometer-tube is obtained from the maker with the instrument, these errors may be avoided and the *true* water-value obtained. Probably a greater error than the above is introduced into ordinary specific-heat determinations by the evaporation of the water in the calorimeter.

II. A second method for the determination of the water-value of the immersed part of a thermometer may be employed,

but it requires that the diameter of the bore of the stem be known. To determine this a fragment of the same thermometer-tube may be obtained from the maker of the instrument, or a short piece of the upper part of the thermometer may be very easily drawn-off before the blowpipe-flame, the closed end of the fragment cut off, and the diameter of the bore measured with a microscope furnished with a micrometer eye-piece and stage-micrometer. Then the weight of mercury (w), corresponding to an increase of temperature from 0° to 100° C., is given by

$$w = al \times 13{\cdot}6, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the area of the tube and l the length in centimetres of 100° ($t°$) on the scale of the thermometer.

The weight (W) of mercury in the bulb is then

$$\mathrm{W} = \frac{w}{\alpha t^{\circ}} + w, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α is the coefficient of apparent expansion of mercury in glass. For lead-glass $\alpha = 0{\cdot}000155$, and for soda-glass 0·0001586. Having thus determined the quantity of mercury, the quantity of glass may be found as in the first method. With a thermometer containing a known weight of mercury, this method gave a water-value for the immersed part of the instrument which was 3·2 per cent. in error. I place much less reliance upon this than upon the former method, as the apparent coefficient of expansion of glass varies more than its specific gravity. The first method is quick and simple, and the results so excellent, that this second method may be almost regarded as unnecessary; but should any case arise in which it is found to possess advantages over the first, it might be possible to determine the coefficient by observing the increase in length of the thermometer when heated in steam.

University College, Liverpool.

XVIII. *On certain Cases of Electrolytic Decomposition.* By J. W. Clark, *Assistant Professor of Physics in University College, Liverpool**.

The atomic or molecular conditions which determine metallic or electrolytic conduction are of great interest, but seem as yet too obscure to allow of any definite general conclusions respecting their nature, beyond regarding a free motion of the particles resulting either from fusion or from solution as necessary for electrolytic conduction. Even this is not without noteworthy exceptions; for Faraday has described some binary compound liquids ($SnCl_4$, $AsCl_3$, &c.†) which neither conduct nor decompose; whilst, on the other hand, some compound solids are known which conduct metallically (Cu_2Se‡, Ag_2Se‡, SnS_2, CuS‡, to which perhaps must be added PbO_2, MnO_2, and Ag_2O), and some bodies which are solid and yet conduct electrolytically (Cu_2S§, Ag_2S‖). Further, zincic iodide‖ neither conducts nor is decomposed when rendered fluid by heat; whilst others (HgI_2‖, $HgCl_2$‖, $PbFl_2$¶) have been considered as conducting without decomposition under the same circumstances. The nature of the conduction of the metallic sulphides is very imperfectly known**.

Whilst thinking over these facts about a year and a half ago, it seemed to me very probable that a careful study of these exceptions to the general laws of electrolytic decomposition might result in more definite conjectures respecting the condition of internal or molecular structure required for conduction and decomposition. To make such a study complete requires the determination and comparison of a number of physical constants (*e. g.* colour, conductivity, expansion, specific and latent heat, refractive index, specific inductive capacity, &c.) for substances which are normal and abnormal in their electrolytic behaviour. This cannot be completely

* Read May 23, 1885.

† Faraday, 'Experimental Researches,' vol. i.

‡ Hittorf, Pogg. *Ann.* Bd. lxxxiv. 1851. § Hittorf (*l. c.*). ‖ Faraday.

¶ Faraday. Beetz (Pogg. *Ann.* Bd. xcii. 1854) has since shown that conduction takes place in a normal electrolytic way. Faraday discovered that the solid Plumbic Fluoride began to conduct below a red heat.

** See Faraday, 'Experimental Researches'; and Hittorf (*l. c.*).

done at present for want of data; but before passing to the consideration of those bodies to which my own investigation refers, I wish to briefly refer to a few previous papers relating to substances of remarkable electrolytic behaviour from this point of view.

Hittorf states that sulphide of silver fuses at a clear red heat, but at a temperature of 180° C. it is sufficiently soft to adapt its shape slowly to that of the surface upon which it rests, and at the ordinary temperature it is malleable: a cast stick of it can be slightly bent without fracture, and it can be cut with a knife or turned in a lathe. This substance has a very low resistance, and even at the ordinary temperatures is electrolytically decomposable by a feeble current. Hittorf (*l. c.*) has concluded, from a long and careful series of experiments upon it, that it conducts electrolytically only, and that its apparent metallic conduction results when a fine thread of metallic silver has formed between the terminals of the sulphide of silver bar.

Hittorf (*l. c.*) has discovered that cuprous sulphide also conducts electrolytically "und besitzt entweder gar keine oder ganz geringe metallische Leitung." Unlike sulphide of silver this body has a high resistance, but, like it, the conductivity increases with increased temperature. Cuprous sulphide melts at a white heat, and may be cast in the form of a rod which at the ordinary temperature is very brittle, although at a "higher" temperature it may be bent.

Hittorf (*l. c.*) points out the difficulty of proving *experimentally* that the conduction of Cu_2S and Ag_2S is *entirely* electrolytic, because the formation of copper or silver by the action of the current in the substance of the bars places their ends in true metallic communication with the battery-terminals.

Cuprous selenide and argentic selenide closely resemble their corresponding sulphur compounds to which reference has just been made, and are described as being "soft" and "slightly malleable" respectively (Watts's 'Dictionary of Chemistry'). Selenides ordinarily closely resemble sulphides in their physical and chemical relations, and are consequently regarded as being possessed of similar molecular constitutions. Hittorf, however, says of cuprous and of argentic selenide,

that "beide sind gute metallische Leiter." Their electrical behaviour is therefore of an exactly opposite nature to that of their corresponding sulphur compounds.

Faraday has noticed that conduction commences in heated electrolytes at very different degrees of liquefaction and softening.

Plumbic chloride * conducts very appreciably at a temperature far below that at which it fuses, and at which it is not noticeably soft. Beetz (*l. c.*) has shown that glass begins to conduct between 200° C. and 220° C., and Dr. Lodge reminds me that this has recently been shown to take place at 100° C.

It appears from the behaviour of these bodies that—

(i.) *In some solid electrolytes there is a sufficient mobility of the molecules at the ordinary temperature to enable electrolytic conduction to take place; in others it is conferred by a rise of temperature which is insufficient to render the solid liquid or even soft. A rise of temperature which is insufficient to render a solid liquid, or so soft as to change its shape, is also sufficient for the equalization of strain as is shown in the annealing of glass. Both electrolytic conduction and the annealing of glass take place more readily at a high than at a low temperature.*

(ii.) *Substances of apparently similar constitution may exhibit opposite forms of electrical conduction* (Cu_2Se, Ag_2Se, and Ag_2S, Cu_2S).

The bodies to which my investigation refers are mercuric chloride and mercuric iodide, which Faraday believed to conduct metallically in the fused condition.

Beetz, as I have recently found, states in a paper, "Ueber die Leitungsfähigkeit für Elektricität welche Isolatoren durch Temperaturerhöhung annehmen" (*l. c.*), that he has obtained evidence of the electrolytic decomposition of fused mercuric iodide; and he attributes its apparent conduction without decomposition to recombination of the products. So far as I am aware, no attempt has been made to examine the nature of the conduction of fused mercuric chloride since Faraday concluded that it probably conducted metallically.

* E. Wiedemann, *Ber. d. Kgl. Sachs. Gesellschaft der Wissenschaften*, 1874. I have unfortunately been unable to refer to this paper; but since the above was written the author has kindly referred me to *Die Elektricitätslehrer* (G. Wiedemann), Bd. i. S. 558, wherein it is stated that the iodide and bromide of lead behave similarly.

Mercuric Iodide.

Mercuric iodide is dimorphic, and at the ordinary temperature forms a scarlet powder which at 110° C. becomes yellow, and at that temperature acquires a very slight electrical conductivity (Beetz). Mercuric iodide melts at 247° C. and boils at 342° C. It is an interesting substance on account of the ease with which it volatilizes at temperatures much below its melting-point; and it is not unlikely that the ease with which the molecules are thus shown to be leaving the solid substance may be connected with a high diffusive rate when it is fused, and this may partially explain the readiness with which the products of its electrolytic decomposition often mix and recombine, thus simulating conduction without decomposition. The mercuric iodide which I have used in the following experiments was prepared either by the precipitation of recrystallized and sublimed mercuric chloride with pure potassic iodide and sublimation of the product, or by the sublimation of the commercially pure substance.

It may not perhaps be out of place to point out, in the first instance, the effect of heat upon mercuric iodide; as it is sometimes stated in text-books of Chemistry that, when heated, it undergoes partial dissociation with liberation of iodine, where the edge of the liquid is in contact with the hot glass vessel. I have, however, convinced myself that this statement applies only to the commercially pure substance, which on sublimation leaves a little impure oxide of iron, and which, on the edges of the glass vessel in which fusion and sublimation are effected, may decompose, yielding free iodine vapour. Pure mercuric iodide may be fused and sublimed without undergoing any such change; nor have I any reason to believe that, when strongly heated in a sealed glass tube, iodine is ever set free, a slight darkening in the colour of the fused substance being the only apparent alteration which it then undergoes.

Here, too, perhaps it may be convenient to describe the preparation of the graphite electrodes, which for some years past I have found very convenient for the decomposition of such substances as act upon platinum. These electrodes are best made from the "leads" of Rowney's HH cedar pencils, which may be easily removed after a few hours' soaking in

water has softened the glue sufficiently to allow of the pencil being split in half. The "lead" is then removed with a knife, and only requires heating to bright redness in a Bunsen-flame (to get rid of the shellac (?) which it contains) to render it fit for use. A platinum wire twisted or bound round one end makes a good connection for the battery-terminals.

When pure mercuric iodide in a sealed glass tube is kept in a state of fusion over a gas-flame, and electrolyzed by means of two platinum-wire electrodes passing through its ends, evidence of its decomposition may be obtained from the iodine set free about the + pole, although no mercury is discoverable at the negative. The quantity of iodine thus set free is, however, small, and does not usually seem to increase with the length of time that the current is allowed to pass; whilst the decomposition, judging from the liberation of iodine vapour about the positive or upper electrode in the tube, appears to take place at temperatures very little above the solidifying-point of the liquid mercuric iodide.

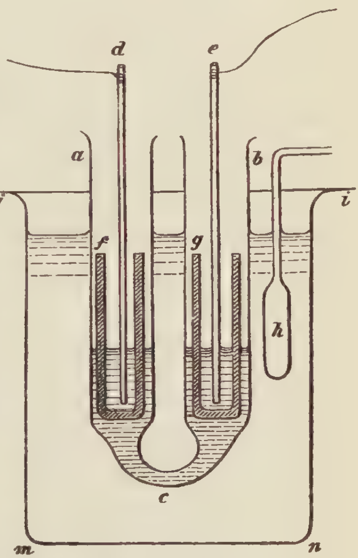
Electrolysis of this substance kept fused in narrow V- and W-shaped tubes over a gas-flame yields much the same results; but in such tubes the resistance is very high, and it is moreover difficult to ascertain precisely what is taking place within them. I therefore adopted a simple V-shaped glass tube of $\frac{5}{8}$ths of an inch diameter and bent at an angle of about 30°, into which was placed a sufficient quantity of mercuric iodide for the experiment. The substance was then kept fused over a gas-flame, and the two graphite electrodes introduced, one at each end of the tube. In such a tube the behaviour of the substance is easily observed; and by blowing air dried over chloride of calcium into the end, the issuing vapours are readily tested for iodine with starch-paper. Under these conditions, I found that when the substance was at a temperature near the melting-point iodine could usually be detected with ease, although at a higher temperature none could be shown to exist in the free state. A control experiment with fused chloride of lead, using a current of the same strength and the same distance between the electrodes, gave evidence of chlorine without difficulty.

Hence it appeared possible that this substance conducted (as Ag_2S had been supposed to do) in two ways—(α) electro-

lytically, at a temperature at which it just became liquid; and (β) metallically, at higher temperatures. But during some observations upon the expansion of fused mercuric iodide in a thermometer-like tube, I noticed that the liquid underwent great contraction during cooling from a temperature a little above the melting-point, accompanied by a distinct loss of fluidity. To the latter change I at once attributed the evidence of electrolytic decomposition, which I had observed at a corresponding temperature, to be probably due, as it would be less favourable to the mixing and recombination of the products of electrolytic decomposition; and I therefore turned my attention to the construction of an apparatus in which they should be so separated as to render this less easy.

The form of apparatus which I finally adopted is shown in section in fig. 1. The tube ($a\,b\,c$) containing two small porous battery-pots ($g\,f$), the graphite electrode, and the mercuric iodide to be electrolyzed, is U-shaped, and the two branches are connected by a constricted portion (c), which further materially hinders the mixing of the fused products of decomposition in the two branches of the tube. This apparatus passes through a hole in the tin cover ($j\,i$) which supports it, and dips into the oil in the beaker, which is heated to the desired temperature by means of a gas-flame or sand-bath, at which it is kept constant by placing the bulb of the air-thermometer (h) in communication with a gas-regulator. When mercuric iodide is electrolyzed in such an apparatus with a current of about 0·02 ampere, iodine is liberated at temperatures far above the melting-point of the substance. If the current was too strong the circuit was usually broken, apparently in consequence of the heat generated at the + electrode volatilizing, or other-

Fig. 1.



J.W.CLARK DEL

wise causing the mercuric iodide to disappear from the porous pot. After passing the current for some hours the gas was extinguished, and when the apparatus had become cool the two branches of the U-tube were cut asunder and broken open for examination. In the + branch, both within and without the porous pot, mercuric iodide and black feathery streaks of iodine were found which gave the starch reaction, and the upper part of the glass tube was coated with volatilized iodine.

Iodine dissolves freely in fused mercuric iodide, producing but little change in the colour of the latter; but just as solidification commences, more or less complete separation seems to take place with the formation of these black patches rich in iodine (and Hg_4I_6?) and an evolution of iodine vapour, which in the previous experiments also helped to lead to the conclusion that electrolytic decomposition occurred only near the melting-point of mercuric iodide.

The contents of the negative branch and porous pot were found to be of a slightly altered colour; but no free mercury was discoverable. Repeated exhaustion of its pulverized contents with absolute alcohol revealed the presence of mercuroso-mercuric iodide (Hg_4I_6 or $2HgI_2$, Hg_2I_2), which might perhaps be inferred to be the first product of the electrolytic decomposition of HgI_2, since it is formed when metallic mercury and mercuric iodide are titurated together in the proper proportions. Mercuroso-mercuric iodide is ordinarily regarded as a distinct compound, and I suppose rightly so; for it can exist without decomposition at a temperature at which mercurous iodide undergoes decomposition with liberation of free mercury; but the stability of this body seems to be greatly increased by the presence of a slight excess of mercuric iodide. Mercurous iodide (Hg_2I_2) dissolves readily in fused mercuric iodide in the proportion to form mercuroso-mercuric iodide. The formation of mercuroso-mercuric iodide by the action of the current upon mercuric iodide may therefore be represented by

$$\text{(i)}\quad 2HgI_2 = Hg_2I_2 + I_2,$$

$$\text{(ii)}\quad 2HgI_2 + Hg_2I_2 = Hg_4I_6;$$

or, considering it to take place in one step,

$$4HgI_2 = Hg_4I_6 + I_2.$$

The action being slow I repeated the experiment, replacing the mercuric iodide in the apparatus just described by some mercuroso-mercuric iodide precipitated nearly according to the equation

$$4KI + I_2 + 2N_2O_4Hg_2O_2 = Hg_4I_6 + 4NO_2KO.$$

The precipitate was then washed, dried, fused, and finally sublimed from an evaporating dish on a sand-bath into a clock-glass which covered it. The substance contained a little mercuric iodide as impurity.

The products of the electrolytic decomposition of this substance are mercury and iodine, of which the former is deposited in the metallic condition, apparently according to the equation

$$Hg_4I_6 = 4Hg + 3I_2;$$

whilst the iodine is absorbed by the Hg_4I_6 in the positive branch of the tube, forming mercuric iodide; thus,

$$3I_2 + 3Hg_4I_6 = 12HgI_2.$$

These results may be summarized as follows:—

The conduction of fused mercuric iodide is electrolytic; but decomposition and recombination may take place so rapidly as to give rise to an apparent metallic conduction; but my investigation gives no grounds for supposing that it does not quantitatively conform to Faraday's Laws.

The causes rendering the proof of its electrolytic decomposition difficult may be summed up as follows:—

(1) *Iodine is soluble in fused mercuric iodide, and so is mercurous iodide, in the latter case with the formation of* Hg_4I_6.

(2) *Mercuric iodide is volatile, and the presence of its vapour renders the detection of free iodine difficult by the ordinary test, and also promotes mixture in the electrolytic apparatus by distillation.*

(3) *It also seems possible that fused mercuric iodide possesses a high diffusive rate, which would further facilitate the mixture and recombination of the products of its electrolytic decomposition.*

(4) *The electrical resistance of fused* HgI_2 *is high.*

When pure mercuric iodide is fused over a gas-flame in a straight glass tube, of about 6 centim. in length and 0·5 centim. in breadth, and electrolyzed between platinum wire or graphite electrodes with a current of about 0·20 ampere, the resistance

shows some remarkable changes. Thus:—In an experiment which I copy from my laboratory journal, the resistance of the mercuric iodide in a sealed tube decreased as the temperature rose, until the needle of the tangent-galvanometer which was included in the circuit stood at 20°; and on allowing the temperature to rise still higher, it fell to 9°. During cooling the inverse change occurred; for on extinguishing the gas and allowing the tube to cool, the needle advanced from 9° to 20° or 21°, and then fell gradually to 0° as conduction ceased. The cause of this change in the resistance is not very clear. I have assured myself that it is not due to any impurity in the mercuric iodide employed, nor is there a sufficient change in polarization of the electrodes at the different temperatures to account for it. With a very feeble current these resistance-changes are not marked, and indeed may escape observation in an experiment such as that which I have described. I believe this effect to be due, first to the formation, and then to the dissociation or other alteration at the higher temperature of the mercuroso-mercuric iodide produced; in support of which it may be stated that mercurous iodide undergoes rapid decomposition with separation of mercury at about the same temperature at which this change of resistance takes place. Perhaps not entirely unconnected with increase of resistance is the heat generated by the current, in consequence of the transition-resistance at the common surface of the + electrode and fused mercuric iodide, which may occasion the formation of vapour on the surface of the electrode. I have observed this give rise to a crepitating noise, and to the formation of a wave-motion spreading from the + electrode over the surface of the fused substance, and, under favourable circumstances, becoming so marked as to throw the whole tube in which the decomposition was being effected into violent oscillation.

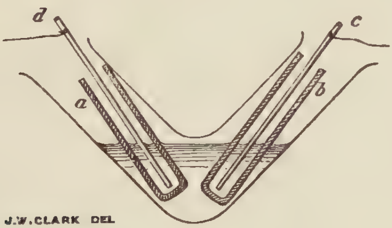
Mercuric Chloride.

Mercuric chloride far exceeds mercuric iodide in the ease with which it volatilizes at temperatures below its melting-point. It melts at 265° C. and boils at 295° C., and is more difficult to decompose with the current than mercuric iodide. This is to some extent due to its higher electrical resistance, which prevents

the use of any complex apparatus designed to represent the products of decomposition and prevent their recombination. The mercuric chloride which was used was prepared by the sublimation of the repeatedly recrystallized pure commercial salt.

The apparatus with which I have succeeded in effecting the electrolytic decomposition of fused mercuric chloride is shown in section in fig. 2, and consists of a glass tube of about $\frac{5}{8}$ths of an inch in diameter bent at an angle of 30°. The porous pots (*ab*) and graphite electrodes (*c d*) project at each end, and the requisite temperature was supplied by the hot sand of a sand-bath. With potassic iodide and starch test-paper the evolution of chlorine at the + pole was readily detected, even when a very feeble current was employed. After the current had been passed through the fused mercuric chloride for some time, the apparatus was allowed to cool, and its contents were subsequently

Fig. 2.



pulverized and exhausted with water, which left an insoluble residue of mercurous chloride (Hg_2Cl_2), which was not entirely confined to the inside of the — porous pot.

Mercurous chloride dissolves in fused mercuric chloride, probably giving rise to a mercuroso-mercuric chloride of analogous composition to some of the well-known double chlorides which mercuric chloride forms. The want of time consequent upon the completion of an investigation on the influence of pressure on electrolytic conduction, upon which I have long been engaged, has prevented my examining this point.

The conduction of mercuric chloride is electrolytic, giving rise to chlorine and mercurous chloride; and there seems no reason to doubt that it conforms quantitatively to Faraday's Law; but the volatility of this substance, as also in the case of

mercuric iodide, and of the products of their decomposition, would render its further proof difficult.

The causes rendering its electrolytic decomposition difficult may be summed up as follows :—

(1) *The volatility of mercurous chloride and its solubility in mercuric chloride.*

(2) *The near melting-* (265° C.) *and boiling-* (295° C.) *points and great volatility of mercuric chloride facilitate the mixing and recombination of the products of its decomposition, and the vapour renders the detection of chlorine by the ordinary test difficult.*

(3) *As previously stated in reference to mercuric iodide, it is possible that the volatility of these substances is connected with a high diffusive rate, when fused, which would facilitate the recombination of the products of its electrolytic decomposition.*

(4) *The electrical resistance of the fused substance is much higher than that of the mercuric iodide.*

Before concluding this paper, I wish briefly to refer to the properties of fused mercuric iodide and chloride with reference to the porous battery-pots in which the electrodes were placed, and which seems sufficiently important to merit a few words of description. These porous pots were 2 inches long, $\frac{1}{4}$ inch in diameter, and varied from $\frac{1}{16}$ inch to $\frac{1}{8}$ thick in the walls. My attention was first attracted to their behaviour by noticing that when they were partially dipped into fused mercuric iodide, that liquid rapidly made its appearance in the pot; and the subsequent analysis of the substance surrounding the porous pots after an experiment, showed the presence of small quantities of the products of the decomposition effected by the current, such as iodine, mercuroso-mercuric iodide, and mercurous chloride. Control experiments with water and with fused plumbic chloride showed that these liquids were unable to penetrate the walls of the porous pots.

The explanation of the facility with which fused mercuric iodide penetrates the walls of a porous pot and rises within it seems to be of a complex nature. The imbibition of this fused substance in the porous walls of the pot is due to capillary action, and does not account for the liquid filling the pot; for

since it is of a capillary nature, this action must cease as soon as the inner surface or wall becomes wetted. In the case of a volatile liquid such as fused mercuric iodide this action may be somewhat prolonged by its volatilization from the inner surface of the pot-wall, and by the direct formation of crystals from the vapour. The subsequent fusion of these crystals will account for the presence of some liquid mercuric iodide within the porous pot, but then this action must cease. Moreover this explanation apparently requires a difference of temperature within and without the porous pot, which, from some special experiments made upon the subject, can scarcely be assumed to exist; and I therefore think that *the explanation of the penetration of the liquid through the walls of the porous pot must be mainly sought in an easy transpiration of the fused mercuric iodide through its pores in consequence of the small initial difference of level ("head") of the liquid.*

I have already stated that analysis showed the presence of some of the products of decomposition formed within the porous pots in the undecomposed substance in which the latter were partially immersed; and this seems attributable to diffusion through the pot-walls. Little seems known respecting the rates of diffusion of fused substances through porous diaphragms; but the particular difficulties in the way of their determination for such volatile substances (which may so readily mix by distillation) seems of itself suggestive of a molecular activity not unconnected with a long free mean molecular path and of rapid diffusion.

XIX. *On the Sensitiveness of Selenium to Light, and the Development of a similar Property in Sulphur.* By Shelford Bidwell, *M.A., LL.B.**

The remarkable property apparently possessed by crystalline selenium of having its electrical resistance varied by the action of light, a property which was first announced by Mr. Willoughby Smith in 1873, has been the subject of many investigations†. Of these the best known, and by far

* Read May 23 and June 13, 1885.

† Willoughby Smith, Journ. Soc. Tel. Eng. ii. p. 31; Earl of Rosse,

the most exhaustive, are the researches of Prof. W. G. Adams and Mr. R. E. Day, an account of which is published in the Phil. Trans. of 1877. As the result of numerous experiments, these gentlemen were led to form the opinion, that "the electrical conductivity of selenium is electrolytic"*. The principal reasons given for this conclusion are:—(1) that the resistance of the selenium-bars used appeared to depend upon the electromotive force of the battery employed, being generally diminished as the battery-power was increased; (2) that the resistance of a bar AB was generally not the same for a current in the direction AB as for a current in the direction BA; (3) that the passage of a battery-current was always followed, when the battery had been disconnected, by a secondary or polarization-current in the opposite direction, it being clearly proved that this secondary current was not due to any thermoelectric action, either in the selenium itself or in any other part of the circuit.

The authors do not, however, appear to have considered that the observed behaviour of selenium was to be explained by actual electrolysis, but rather that the molecular structure or crystalline condition of the substance was altered or modified by the action of a current of electricity in such a manner as to produce effects analogous to those which would have occurred if the selenium were an electrolyte and actually decomposed by the current. As to the possible influence of light, the following are their words †:—"Light, as we know, in the case of some bodies, tends to promote crystallization, and when it falls on the surface of such a stick of selenium, tends to promote crystallization in the exterior layers, and therefore to produce a flow of energy from within outwards, which, under certain circumstances, appears in the case of selenium to produce an electric current. The crystallization

Phil. Mag. March 1874, p. 161; Sale, Proc. Roy. Soc. 1873, p. 283; Phil. Mag. March 1874; Werner Siemens, Phil. Mag. November 1875, p. 416; Draper and Moss, 'Chemical News,' xxxiii. p. 1; Adams and Day, Proc. Roy. Soc. 1876, p. 113; Phil. Trans. 1877, p. 313; C. W. Siemens, Proc. Roy. Inst. 1876, p. 68; Sabine, Phil. Mag. June 1878, p. 401; Graham Bell, 'Nature,' xxii. p. 500; Shelford Bidwell, Phil. Mag. April 1881, and January 1883; Fritts, 'Electrical Review,' March 7, 1885, p. 208.

* Phil. Trans. vol. 167, p. 328; Proc. Roy. Soc. 1876, p. 115.

† Proc. Roy. Soc. 1876, p. 117.

produced in selenium by light may also account for the diminution in the resistance of the selenium when a current from a battery is passing through it, for, in changing to the crystalline state, selenium becomes a better conductor of electricity."

Attention has lately been again directed to the subject of selenium, and its behaviour under the influence of light, by the publication, by Mr. C. E. Fritts of New York, of a new and extremely ingenious method of constructing selenium cells*. He melts a thin film of selenium upon "a plate of metal with which it will form a sort of chemical combination . . . . . During the process of melting and crystallizing, the selenium is compressed between the metal plate upon which it is melted and another plate of steel or other substance with which it will not combine. . . . . The non-adherent plate being removed after the cell has become cool, [he] then covers that surface with a transparent conductor of electricity, which may be a thin film of gold-leaf. . . . . The whole surface of the selenium is therefore covered with a good electrical conductor, yet is practically bare to the light, which passes through the conductor to the selenium underneath." The sensitiveness to light of cells constructed in this manner seems to be far in excess of anything that has been previously obtained; and the "photoelectric" currents which (like the selenium bars of Messrs. Adams and Day) they are capable of originating, are said to be strong enough to be actually useful in practical work.

It is impossible to read Mr. Fritts's paper without being impressed by the resemblance of some of the phenomena which he describes to those of electrolysis. The mere arrangement of the apparatus—two metallic plates with a third substance between them—is in itself strongly suggestive; while the unequal resistance offered by the two surfaces, and the generation of an independent electromotive force, in conjunction with the polarization-effects above referred to†, make it

* Proc. American Assoc. 1884. Reproduced in the 'Electrical Review,' March 7, 1885, p. 208.

† "The existence of polarization," says Clerk Maxwell, "may be regarded as conclusive evidence of electrolysis." 'Electricity,' vol. i. p. 363.

hard to believe that the conduction of selenium (in the form used in experiments) is not truly and literally electrolytic.

The only considerable difficulty in the way of this hypothesis arises from the fact that selenium is not an electrolyte. Ever since its discovery in 1817, selenium has been regarded as an element, and very strong evidence indeed would be necessary to deprive it of its elementary character ; this is perhaps the reason why the electrolytic theory has not previously been proposed. But there is a possible way out of the difficulty, which was suggested to me by the first words in the above quotation from Mr. Fritts's paper. He spreads the selenium upon a plate of metal *with which it will form a chemical combination*. Now selenium will, I believe, combine more or less easily with all metals, forming selenides; and in experiments upon the conductivity of selenium, it has been usual to submit the substance to prolonged heating in contact with metallic electrodes. This prolonged heating (generally followed by slow cooling) has hitherto been called "annealing;" and the undoubted fact that it diminishes the specific resistance of the selenium and increases its sensitiveness to light, has been explained by supposing that the process is favourable to perfect crystallization.

I venture to suggest, as the true explanation of the effect, that heating is favourable to a chemical combination between the selenium and the metal forming the electrodes, that a selenide is thus formed which completely surrounds the electrodes, and is perhaps diffused to some extent throughout the mass of the selenium*; and that the apparently improved conductivity of the selenium, together with the electrolytic phenomena which it exhibits, are to be accounted for by the existence of this selenide.

I have sometimes been tempted to think it possible that the apparent conductivity of selenium may in fact be *entirely* due to the impurities which it contains, and that perfectly pure selenium would be as good an insulator when in the crystalline form as it is in the vitreous condition. Vitreous selenium might contain a large percentage of conducting particles without sensible increase of its conductivity, but that this would not be the case with crystalline selenium, is rendered

* The selenium is necessarily for some time in a liquid state.

more than probable by the results of some experiments which I have described in a former communication*. If a conducting powder, such as graphite, is mixed with melted sulphur, even in small proportions, the mixture when cold is found to conduct electricity; while if a very large proportion of the same powder is incorporated with melted shellac, the shellac when cold remains sensibly as perfect a nonconductor as if it were pure. The explanation which I have given of these facts, and in support of which a number of experiments are quoted, is as follows:—The first mixture does not consist of a uniform structureless mass of sulphur, having particles of carbon imbedded in and completely surrounded by it: it is in fact an aggregation of little crystals of sulphur with carbon packed between them like mortar between bricks. The conduction thus takes place entirely through the carbon particles, which may be considered as extending in a series of chains from end to end of the mass. In the case of the shellac mixture, though the proportion of carbon may be larger than in the sulphur experiments, the resistance is still sensibly infinite, because the structureless shellac penetrates between and completely surrounds the carbon particles. Just in the same manner, selenium, when in the vitreous condition, would completely surround any particles of conducting selenides which it might contain; while, when the selenium was crystallized, the conducting particles would arrange themselves in the form of a network, capable of conveying a current of electricity.

Selenium which is free from impurities appears not to be an article of commerce. An analysis of samples collected by Professor Graham Bell from different parts of the world disclosed the presence of the metals iron, lead, and arsenic†, all of which would form conducting selenides. Nevertheless I thought it would be worth while to ascertain roughly the specific resistance of a piece of selenium which, since it has come into my possession, has never been in contact with metal. The selenium (which was supplied by Messrs. Hopkin and Williams) was melted in a mould built up of slips of glass,

* Phil. Mag. May 1882, p. 347.

† Paper read before the National Academy of Sciences, April 21, 1881.

crystallized and "annealed" in the usual way; but, contrary to the general practice, it was *not* fitted with metallic electrodes before annealing. A plate of crystalline selenium was thus formed, having a thickness of about 2 millim. and a superficial area of 1 square centim. The two opposite surfaces were rendered smooth and clean by rubbing them upon a flat board covered with fine glass-paper, and the plate was placed between two layers of thick tinfoil which were pressed into good contact with it by a weight of 500 grammes. When this arrangement was connected in circuit with 6 Leclanché cells and a reflecting galvanometer, a deflection was produced indicating a current of about $\frac{1}{50}$ micro-ampere. Assuming the electromotive force of the battery to have been 10 volts, the resistance of the plate would be 500 megohms; and therefore the resistance of a cubic centimetre of the selenium between opposite faces (*i. e.* its specific resistance) would be 2500 megohms. From the dimensions and resistance of a good selenium cell with copper electrodes, which I have in my possession, I calculated that the specific resistance of the selenium contained in it was about ·9 megohm. Thus, so far as the result of a single rough experiment can be trusted, it appears that the conductivity of selenium which has been annealed in contact with copper is nearly 3000 times greater than that of selenium which has undergone similar treatment without the presence of a metal. Whether selenium, when perfectly pure, is altogether a non-conductor, would be an interesting question for an expert chemist to determine *. It is sufficient for the theory which I am at present advocating that its specific resistance should be very high.

By assuming the admixture with the selenium of metallic selenides, an explanation is afforded of the following facts:—

(1) The diminished resistance produced by annealing.

(2) The fact, first pointed out by Graham Bell, that the resistance of selenium appears to depend greatly upon the nature of the metals of which the electrodes are formed. For obtaining low resistance he recommends the use of brass in preference to platinum, and expresses his belief that the chemical action between the brass and selenium contributes to

* On more mature consideration I am inclined to think that it is *not*.

the low resistance of his cells, "by forming an intimate bond of union between the selenium and brass." *

(3) The fact observed by Adams and Day that there is generally a "diminution of resistance in the selenium as the battery-power is increased." The same phenomenon occurs in the mixtures of sulphur and carbon before referred to. It points to the existence of imperfect contact between conducting particles, the conduction partaking of the nature of disruptive discharge, and is consistent with the supposition that particles of conducting selenide are imbedded in the selenium †.

(4) The apparent production by a current through a piece of selenium of a "*set* of the molecules which facilitates the subsequent passage of a current in the opposite, but obstructs one in the same direction"‡. This would be accounted for by the electrolytic deposition of selenium (from the selenide) upon the anode.

(5) The polarization-effects, which would also proceed from electrolysis.

(6) "A slight increase of temperature of a piece of annealed selenium is accompanied by a large increase of electrical resistance"§. This also occurs in the mixture of sulphur and carbon, and is explained by supposing that the heat-expansion of the medium draws apart the conducting particles contained in it, causing them to have fewer points of contact with each other, and thus increasing the resistance of the whole ‖. A more considerable rise of temperature so greatly diminishes the specific resistance of the selenide (and perhaps of the selenium) as to more than counterbalance this effect; and thus it happens (as I have shown in a former communication ¶) that selenium cells have a "temperature of maximum resistance," which is generally a few degrees above the average temperature of the air.

* Lecture to American Assoc. 1880. Reprinted in 'Nature,' vol. xxii. p. 500.

† See "On the Electrical Resistance of Carbon-contacts," Proc. R. S. Feb. 1, 1883; and "On Microphonic Contacts," Journ. Soc. Tel. Eng. April 12, 1883.

‡ Adams and Day, Proc. R. S. 1876, p. 114.

§ Adams and Day, Phil. Trans. 1877, p. 342. See also Phil. Mag. Jan. 1883, p. 31.

‖ Phil. Mag. May 1882, p. 351. ¶ Phil. Mag. April 1881.

(7) The resistance of prepared selenium is generally greatly diminished by the action of time. Prof. Adams found that the average resistance of a number of pieces of selenium was reduced to less than one fortieth in the course of a year *. During this period the selenium had been in contact with the metallic electrodes; and it seems possible that a larger quantity of selenide than was produced in the first instance by the process of annealing was slowly formed. This would especially occur at the "marked end," or anode, where there would naturally be a quantity of free selenium.

In the above argument it has been assumed that selenium will combine directly with any metal with which it is brought into contact, the combination being facilitated by the application of heat. In the case of such metals as copper, brass, and silver this is undoubtedly the fact. Indeed, an attempt to make a selenium cell with silver wires was attended with failure in consequence of the complete destruction of the metal after contact with the melted selenium for only two or three minutes. It is, however, questionable whether platinum (which was the metal used by Adams and Day) is, in any sensible degree, attacked by selenium either at the ordinary temperature or at that reached in the process of annealing. With sufficient heat the two substances will undoubtedly unite; and I have found that the surface of platinum-foil upon which melted selenium has been kept for an hour or two at a temperature probably of about 250° C. acquires a bluish-grey colour which may be due to selenide. But whether any appreciable quantity of selenide is formed in the ordinary preparation of crystalline selenium is a question only to be settled by the aid of refined chemical operations which I am incompetent to undertake, and in the meantime the suggested theory is left without direct confirmation.

But certain indirect evidence in support of my views has been forthcoming. Selenium is an element which, in its properties, closely resembles sulphur, and attempts have from time to time been made, hitherto without success, to develope in sulphur that peculiar sensitiveness to light which is such a remarkable characteristic of selenium. It occurred to me that if this property of selenium were really due to the acci-

* Phil. Trans. *loc. cit.* p. 348.

dental existence of metallic selenides, then the admixture with sulphur of metallic sulphides might be expected to lead to similar effects. It is not possible to "anneal" a stick of sulphur or a sulphur "cell" previously furnished with metallic electrodes, because sulphur does not, like selenium, solidify and crystallize at a higher temperature than that of its first melting-point. But if it is true that the virtue of annealing really lies in the fact that a chemical union of the two elements is promoted by the action of heat, it is clearly immaterial whether the substances are heated together before or after the formation of the cell. Sulphur containing sufficient metallic sulphide to render it a conductor of electricity might be used in the construction of a cell which might be expected to be sensitive to light without any preliminary annealing. This turned out to be actually the case.

Silver was the metal chosen for the experiments on account of the facility with which it combines with sulphur.

Cell No. 1.—Five parts of sublimed sulphur and one part of precipitated silver were heated together in a porcelain crucible for about two hours. The mixture was from time to time stirred with a glass rod and was finally allowed to settle, so that the bulk of the sulphide and any free silver which might remain fell to the bottom of the crucible. When the temperature was slightly above the melting-point the liquid sulphur, which was perfectly mobile, though black with minute suspended particles of sulphide, was poured off for use. Two wires of fine silver* were then coiled side by side around a strip of mica 50 millim. long and 27 millim. wide; the wires were about 1 millim. apart, and care was taken that they did not touch each other at any point. Some of the melted sulphur was spread evenly over one surface of the mica, the two wires being thus connected with each other through half their entire length by a thin layer of the prepared sulphur. When cold, this cell was connected in circuit with a battery and a galvanometer. It was found to conduct electricity, but its resistance was very high, being probably between 20 and 30 megohms. With the object of partially bridging over the intervals between the wires, the sulphur was melted by laying the cell upon a hot plate, and a piece of very thin

* Supplied by Messrs. Johnson and Matthey.

silver-foil, measuring 25 millim. by 10 millim., was laid upon its surface: this was probably entirely converted into sulphide before the cell was again cold. The cell was now found by a bridge-measurement to have a resistance of 900,000 ohms *. Once more it was connected with a Leclanché cell and a suitably shunted galvanometer; the deflection was noted, and a piece of magnesium wire was burnt at a short distance from the sulphur. The deflection was immediately more than doubled; and when the magnesium was extinguished, the spot of light at once returned to very nearly its original position. The effect was almost as great when a glass trough containing a saturated solution of alum was interposed between the sulphur and the burning magnesium †.

Now it is well known that the resistance of sulphide of silver is greatly diminished by heat ‡, and it was therefore important to ascertain whether the effect just described was due to light or to heat. To speak more accurately—Is it an effect of *radiation* or of *temperature?* Exposure to radiation, whether visible or invisible, is of course always accompanied by a certain rise of temperature, and confusion has sometimes arisen, especially in discussing the properties of selenium, from failure to distinguish between the direct effects of radiation, and the indirect effects which are primarily due merely to a rise of temperature §. In the photographic processes it is radiation *per se* that produces the observed results: in the best known processes, the effective rays happen to be those which correspond to the most-refrangible part of the visible spectrum together with the invisible rays beyond it. But by more recently discovered methods the "obscure heat-rays," as they are sometimes called, have been made available for photographic purposes ‖; and these do not act by virtue of any rise of temperature which they may cause, but exert

* This resistance was afterwards found to be very variable, and it was never the same with a direct and a reverse current.

† This cell was exhibited in action at the Meeting of the Physical Society on May 23rd, and at the Soirée of the Royal Society on June 10.

‡ Faraday, Exp. Res. §§ 432–439.

§ See Moser, Proc. Phys. Soc. 1881, p. 348.

‖ Captain Abney is said to have obtained a photograph of a kettle of boiling water by means of the invisible radiations which it emitted.

direct chemical action upon the sensitized plate. Again, if a thermo-pile is exposed to radiation, an electromotive force is generated. Here, however, the effect of radiation is indirect; it acts only through the medium of the heat which it produces; and if an equal and similarly distributed amount of heat were communicated to the thermo-pile by any other means (as by conduction), exactly the same effect would follow. In an ordinary selenium cell radiation acts both directly and indirectly, tending to produce opposite effects. The direct effect of the radiation, whether it be visible or infra-red or ultra-violet, is a diminution of the resistance of the cell; at the same time the radiation slightly raises the temperature of the cell, and so indirectly tends to increase its resistance. If a selenium cell in circuit with a battery and a galvanometer is suddenly exposed, by withdrawing a screen, to the radiation of a black-hot poker, a momentary swing of the galvanometer-magnet will at first indicate a fall in the resistance; but this will be almost immediately followed by a rise which will increase up to a certain limit as the temperature of the cell becomes higher. The same kind of thing occurs when the cell is exposed to the infra-red or red portions of the spectrum; but in the latter case the temperature-effect merely diminishes, instead of overpowering, that directly due to radiation. If the bridge method is used for measuring the resistance, it may easily happen that the effect of gradually rising temperature escapes notice, a balance not being obtained until the temperature has become constant; and thus, probably, is to be explained the fact that different observers have attributed the most powerful action upon selenium to different parts of the spectrum, ranging from infra-red to greenish yellow.

The resistance of the sulphur cell which has been described, unlike that of most selenium cells, was diminished by a rise of temperature *. When in circuit with a Leclanché cell and a galvanometer, the effect of holding a nearly red-hot brass rod at a distance of 3 centim. from its surface, was a gradual fall of resistance, which in 15 seconds was indicated by 23 scale-divisions. When the rod was removed,

* This was not so with all the cells subsequently made. See description of cell no. 3 below.

the spot of light slowly returned to its original position, occupying several seconds in doing so. It is certain that the temperature of the sulphur must in this experiment have been much higher than when it was exposed to burning magnesium, with a solution of alum interposed, yet the effect was very much smaller; moreover, it was gradual instead of instantaneous.

Another experiment seems to prove conclusively that the resistance of the cell is diminished by the direct action of radiation, quite apart from any effect which may be produced by an incidental rise of temperature. On a cloudy day the cell, with the alum trough before it, was placed at a distance of 16 feet from a small window, all the other windows in the room being darkened. With the same battery and galvanometer as before, it was found that closing the window-shutter caused an instantaneous swing of the spot of light through 90 scale-divisions in the direction indicating increased resistance; and when the shutter was again opened, there was immediately an equal swing in the opposite direction. A delicate thermopile of 54 pairs, connected with an astatic reflecting-galvanometer of low resistance, was then put in the place of the sulphur cell, and the alum trough placed before the open end of the conical reflector attached to it. On opening the window-shutter, a deflection occurred indicating a current which was found by trial to be equal to that produced by the radiation of the human body at a distance of 10 ft. 6 in. It is needless to say that such a minute change of temperature as this implies was without sensible effect upon the resistance of the sulphur cell. There can then be no doubt whatever that the whole of the observed effect of the light upon the sulphur was due to the action of radiation as such, any change of resistance resulting from the incidental rise of temperature being quite inappreciable.

Cell No. 2.—This was constructed in a somewhat different manner. A piece of silver-foil was laid upon the surface of the mica before the two wires were wound round it, and instead of having prepared sulphur spread upon one face, the whole was immersed in *pure* melted sulphur for a few minutes, and then carefully drained. Before this treatment the silver wires were of course short-circuited by the foil, but the liquid

sulphur penetrated between them, forming a film of sulphide; and when cold, the resistance of the cell was about 100,000 ohms. Though this cell turned out to be somewhat less sensitive than the other, it seemed likely that, on account of its comparatively low resistance, it might be successfully used for a photophonic experiment. It was therefore connected in circuit with a battery of ten Leclanché cells and a telephone, and exposed to a rapidly interrupted beam of light. The telephone at once gave out a musical note, which was nearly as loud as that produced by a good selenium cell under similar circumstances.

The behaviour of this cell under changes of temperature was the same as that of the other.

Cell No. 3.—A mixture, consisting of equal parts of sublimed sulphur and precipitated sulphide of silver, was melted and spread on one surface of a slip of mica, around which two silver wires had been wound as before. No foil was used in this case. The resistance of this cell was diminished by radiation, but increased in a very marked manner by rise of temperature. A paraffin lamp, at a distance of 18 inches, produced a steady diminution of the resistance. When the lamp was placed at a distance of 10 inches, the galvanometer-needle first moved in a direction indicating a further fall of resistance; but after a few seconds, when the temperature began to rise, it turned in the opposite direction. On moving the lamp 6 inches nearer, there was at once a large deflection in the direction of increased resistance, the temperature-effect completely predominating over that of radiation.

Cell No. 4.—A strip of silver-leaf was attached to a glass plate by means of gold size, and the middle part of it was exposed to the vapour of boiling sulphur until both surfaces were completely blackened. The resistance of this cell was high, but for a few days it was extraordinarily sensitive, a reflected beam of sunlight instantly effecting a diminution of 80 per cent. in its resistance. About a fortnight after it was made, its sensitiveness had greatly fallen off.

All these cells resemble selenium in giving polarization-currents after being detached from the battery.

Supposing it to be true, then, that it is not in the selenium

or sulphur itself, but in certain metallic selenides or sulphides, that the sensitiveness to light is resident, does it become easier to explain the phenomenon, or, rather, to deprive it of the unique position which it has hitherto appeared to hold, and assign to it a place among a class of analogous effects?

I believe that, at all events in the case of the sulphur-silver cell, it is principally at the surface of the *electrodes* that the effects of radiation are to be looked for.

If a current of electricity is passed through a mass of sulphide of silver having silver electrodes, silver will be deposited upon the cathode and sulphur upon the anode. The accumulation of silver upon the cathode will clearly produce no appreciable effect upon the conductivity of the arrangement, and need not be considered. But sulphur has an enormously high resistance, and the deposition of a mere film of free sulphur upon the anode would be sufficient to stop the current altogether. The current is not in fact stopped, because the deposited sulphur at once combines with the silver of the anode, merely adding a new layer to the electrolyte. Thus the metal of the anode gradually combines with the sulphur of the electrolyte; and the conductivity of the arrangement will depend to a great extent upon the facility with which this combination is effected, the quantity of electricity which can pass in a given time being limited by the quantity of sulphur which is capable of uniting with the electrode in the same time.

Sulphur combines with silver far more readily than with iron. If, therefore, my views are correct, we should expect a cell with an iron anode to offer a much greater resistance than one which had an anode of silver, the material of the cathode, so long as it was a good elementary conductor of electricity, being of comparatively little importance. To test this idea, a cell was made consisting of electrodes of iron and silver imbedded in a mixture of sulphide of silver and sulphur. The cell being connected with a battery and a galvanometer, the deflection was 115 divisions when the current passed from the silver to the iron through the electrolyte, and only 4 divisions when the direction of the current was from iron to silver*.

* The resistance of the galvanometer was 3483 ohms, and it was shunted with a coil of 20 ohms. The resistance of the Leclanché cell was about 5 ohms.

The resistance was therefore nearly 30 times as great with an iron anode as with a silver anode. It is clear that this was not the result of bad contact between the iron and the electrolyte (such as was supposed by Graham Bell in the analogous case of selenium to account for the high resistance of a cell with platinum electrodes as compared with one in which the electrodes were made of brass), because such an effect would be independent of the direction of the current. Rather it seems that the resistances of the two anodes afford data for measuring the relative facilities with which sulphur combines with silver and with iron.

Assuming it to be thus experimentally proved that the resistance of a sulphur-silver cell depends largely upon the readiness with which sulphur unites with the anode, it follows that any cause which would assist this union would at the same time diminish the resistance. Now it is well known that certain chemical combinations are accelerated by the action of radiation—the explosive union of chlorine with hydrogen under the influence of sunlight being a familiar example. The question then suggests itself, Does sulphur combine with silver more readily when exposed to radiation than it otherwise would? There is, I believe, direct evidence that it does.

A glass plate, covered with silver leaf, was placed, with the silvered side downwards, over a crucible of boiling sulphur. One half of the plate was covered with a piece of black cloth, and the arrangement was exposed to bright sunshine. In a short time the visible portion of the silver was darkened, owing to its partial conversion into sulphide; the cloth was then removed, and the silver beneath it was found to be scarcely discoloured. There was a distinct line of demarcation between the two halves. The experiment was repeated with the same result.

Since this effect might possibly have been due to other causes than the action of light (such as the unequal condensation of sulphur vapour upon the covered and uncovered portions of the plate), the experiment was made in another form. A piece of silver leaf attached to glass was brushed over with a solution of sulphur in bisulphide of carbon; and in order to keep the temperature low and uniform, the silvered glass plate was immersed in a basin containing cold water,

which was placed in the sunshine. A board was laid across the top of the basin so as to shade one half of the plate, the other half being exposed to the direct rays of the sun. In a quarter of an hour the exposed portion of the silver had acquired a dark brown colour, while that which had been protected was of a pale yellow tint, the outline of the shadow of the board being sharply defined. I think we have here the strongest evidence that the combination of sulphur with silver is assisted by radiation.

But it is not perhaps necessary to assume that the effective action of light is confined entirely to the surface of one of the electrodes. If, as is commonly believed, electrolytic conduction involves a series of decompositions and recompositions throughout the electrolyte, any cause which assists either the separation or recomposition (or both) of the components of the electrolyte might be expected to increase its conductivity; and it seems reasonable to suppose that the same influence which would assist the union of two substances when they have a tendency to unite would also be favourable to their separation when they have a tendency to separate. It is not impossible, therefore, that radiation, acting upon the surface of a thin layer of sulphide of silver through which an electric current is passing, might, by facilitating the molecular rearrangement of the atoms of sulphur and silver, exert a material influence upon the conductivity of the sulphide*.

So far as regards the explanation of the effect of light upon the resistance of selenium, I am aware that this paper contains little more than speculative suggestions, which are at present almost entirely unsupported by experimental evidence†. It is, however, noteworthy that these speculations led to the construction of a cell which, without containing a particle of selenium, behaved almost exactly as if it were composed of that substance. How far this may be considered to prove

* There are some experimental reasons, into which I am not at present prepared to enter, for believing that the admixture with the sulphide of a certain amount of free sulphur is necessary for the development of sensitiveness to radiation.

† It is especially desirable to ascertain experimentally whether the combination of selenium with the metals used as electrodes in selenium cells is assisted by light.

anything with regard to selenium I do not know; but in any case the discovery of another substance possessing the same remarkable property seems in itself to be a matter of some interest.

XX. *On the Error involved in* Professor Quincke's *Method of Calculating Surface-Tensions from the Dimensions of Flat Drops and Bubbles. By* A. M. WORTHINGTON, *M.A., Clifton, Bristol**.

IN one of a series of well-known papers (Pogg. *Annal.* vol. cxxxix. part 1; and Phil. Mag. April 1871) Prof. Quincke has recorded a large number of measures of flat drops and bubbles, from which he has deduced the value of the tensions, not only at the free surface of liquids, but also at the common surface of two liquids in contact.

The numerical results obtained exceed very appreciably the values of the surface-tensions deduced from observations with capillary tubes, and Prof. Quincke attributes the difference partly to the exposure of the surface of the meniscus in capillary tubes to atmospheric impurities, but chiefly to the fact that with capillary tubes the edge-angle is not zero, and that the quantity measured is not the surface-tension of the liquid, but the surface-tension multiplied by the cosine of the edge-angle. Thus a special significance has been attached to the high values obtained by the method of flat drops or bubbles, and these values have been widely copied and made the basis of numerical calculations.

The calculation of the results involves the integration of the equation to the liquid surface

$$T\left(\frac{1}{R}+\frac{1}{R'}\right)=Dz.$$

Prof. Quincke starts by writing $\frac{1}{R'}=0$, *i. e.* by assuming that the drop or bubble may be treated not only as flat at the vertex, but also as having an infinite diameter. It is true that in § 5 of the paper referred to he himself comments on the

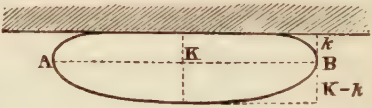
* Read June 13, 1885.

fact that these assumptions are only approximately correct; but he does not attempt to show that the error entailed by these two assumptions is insignificant. It is the object of this paper to show that the error is very considerable, amounting in most cases to as much as 10 per cent. of the whole value, and that when duly corrected the values obtained by this method do not appreciably exceed those obtained with capillary tubes.

Prof. Quincke's process consists in measuring by means of a cathetometer-microscope the dimensions of a large drop or bubble, such as is represented in section in figs. 1 and 2, that has been placed on, or below, a horizontal glass plate.

Fig. 1.

Fig. 2.



The dimensions measured are

(1) The distance K of the vertex from the plate.

(2) The distance k of the section of maximum radius from the plate.

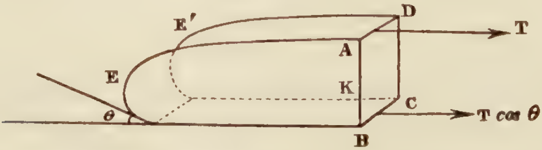
(3) The maximum diameter AB.

The first two measures afford the value $K-k$ of the distance between the vertex and the section of maximum radius, and the last affords the value L of the maximum radius.

The physical meaning of the assumptions made in the calculation may be explained in the following manner.

Imagine a central slab to be cut out of the drop between two parallel vertical planes at small unit distance apart, and that the slab is again cut in half at right angles to its length, so that we realize the portion ABCDE′E of the diagram (fig. 3).

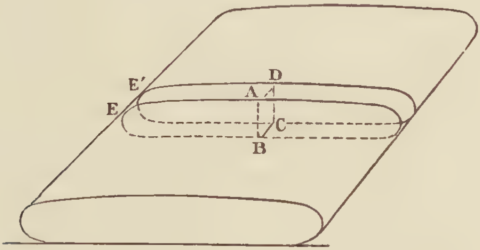
Fig. 3.



If the drop were of infinite radius, and therefore flat at the top, the slab thus obtained would be equivalent to a similar

slab cut out of a mass of liquid, shaped as in fig. 4. If we now, on this supposition, consider the equilibrium of the mass represented in fig. 3, with reference to horizontal forces parallel to its length, we can equate the hydrostatic pressure

Fig 4.



on the rectangular end to the sum of the tensions exerted along the two edges AD and BC. Thus writing, with Quincke, AB=K, and writing D for the difference between the density of the drop or bubble and that of the surrounding medium,

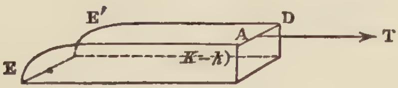
$$T+T\cos\theta=\frac{K^2D}{2};$$

whence, when $\theta=0°$,

$$T=\frac{K^2D}{4}.$$

Or, if we consider the equilibrium of that portion only of the slab which lies above the horizontal section of greatest area (see fig. 5), we may equate T to the hydrostatic pressure on the rectangular area of unit breadth and depth $(K-k)$,

Fig. 5.



whence
$$T=\frac{(K-k)^2D}{2}. \quad \ldots\ldots\ldots \quad (1)$$

It is from this equation that Prof. Quincke calculates the value of T. It is evident that in neglecting the curvature of the vertex we are neglecting the pressure due to this curvature transmitted to the whole area $K-k$. Thus, if b be the radius of curvature in question, the pressure disregarded is

$\frac{2T}{b}(K-k)$. The surface-tension T has to balance this as well as the hydrostatic pressure due to the weight of the liquid, and neglect of this term will lead to too small a result.

Again, in neglecting the curvature in the plane at right angles to the plane of the diagram, we evidently leave out of account the tension exerted along each edge AE, DE′, of the slab, which produces a pressure $\frac{T}{R'}$ on each unit area of the surface.

Since the surface is one of revolution, R′ is the length of the normal intercepted by the axis, and writing ϕ for the inclination of the normal to the axis measured on the side of the vertex, *i. e.* for the *edge-angle* of the drop- or bubble-forming fluid at any horizontal section, we have $\frac{1}{R'}=\frac{\sin\phi}{x}$, where x is the horizontal radius of the section; and the pressure on a horizontal strip of the rectangular end of elementary depth dz is $\frac{T\sin\phi\, dz}{x}$ and the total action omitted,

$$\int_0^{K-k}\frac{T\sin\phi\, dz}{x};$$

so that the complete equation is

$$T=\frac{(K-k)^2D}{2}+\frac{2T}{b}(K-k)-T\int_0^{K-k}\frac{\sin\phi\, dz}{x} \quad . \quad . \quad . \quad . \quad (2)$$

The value of the integral of the last term to a first approximation is shown by Laplace (*Méc. Céleste*, livre x. 2ᵉ Suppl. p. 483), or by Mathieu (*Théorie de la Capillarité*, p. 137) to be

$$\frac{4a}{3}\cdot\frac{1-\cos^3\frac{\phi}{2}}{x},$$

where $a=\sqrt{\frac{T}{D}}$.

When x is equal to the maximum radius L, then $\phi=90°$, and the term becomes

$$T\times\frac{4a}{3L}\left(1-\frac{1}{2\sqrt{2}}\right).$$

We may use for (a) in this corrective term the value given by the approximate equation (1),

$$T=\frac{(K-k)^2D}{2};$$

whence

$$\sqrt{\frac{T}{D}}=a=\frac{K-k}{\sqrt{2}}.$$

Thus the term in question reduces to

$$2T\frac{K-k}{3\cdot282L};$$

and the complete equation (2) becomes

$$T=\frac{(K-k)^2}{2}D+\frac{2T}{b}(K-k)-\frac{2T(K-k)}{3\cdot282L};$$

or

$$\frac{T}{D}=\frac{(K-k)^2}{2}+\frac{T}{D}2(K-k)\left(\frac{1}{b}-\frac{1}{3\cdot282L}\right).$$

Or, writing $-C$ for the value of the factor $\left(\frac{1}{b}-\frac{1}{3\cdot282\,L}\right)$ in the corrective term,

$$\frac{T}{D}=\frac{(K-k)^2}{2(1+2\overline{K-k}C)}. \quad . \quad . \quad . \quad . \quad (3)$$

To find the value of C we must know that of $\frac{1}{b}$. This is shown by Laplace (*loc. cit.* p. 485) or Mathieu (*loc. cit.* p. 140) to be equal to

$$2\sqrt{2}a^{-\frac{3}{2}}\sqrt{\pi x}\tan\frac{\phi}{4}e^{-\frac{x}{a}-4\sin^2\frac{\phi}{4}};$$

which, when $x=L$ and $\phi=90°$, reduces to

$$\frac{1}{b}=\sqrt{\frac{8\pi L}{a^3}}\times\cdot4142136\times e^{-\frac{L}{a}+\cdot585788},$$

in which we may use for a the mean value of $\frac{K-k}{\sqrt{2}}$ found by Prof. Quincke.

Before giving the numerical results, it is necessary to observe that the value of the integral $\int_{z=0}^{z=K-k}\frac{\sin\phi\,dz}{x}$ is calculated

on the assumption that the fraction $\frac{a}{L}$ is small; and, again, the value of $\frac{1}{b}$ is calculated on the assumption that $\frac{dz}{dx}$ is small, even when x is large, *i. e.* that the drop is very flat, even far from the vertex. Now the drop or bubble used by Prof. Quincke was often far from satisfying these conditions. In some cases the diameter was so small that the fraction $\frac{a}{L}$ amounted to as much as ½, and the curvature at the vertex was so considerable that the value of $\frac{1}{b}$ cannot be satisfactorily calculated in the way described. Thus in the first measure of an air-bubble in water (Quincke, *loc. cit.* § 3, table III.) $\frac{a}{L} = \cdot 319$; while in the case of drops of petroleum in water it is as much as ·3768.

I have therefore selected for correction only those measures for which the value of $\frac{a}{L}$ was smallest, though the mean value of the observed quantity $K-k$ used in calculating $\frac{1}{b}$ was generally taken from the whole of the measures given by Prof. Quincke.

Air-bubbles in Hyposulphite of Soda.

$D = 1\cdot 1248.$

No.	L.	$K-k$.	$\frac{1}{3\cdot 282\,L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
3.	1·41	·3738	·2161	·0492	·07856	·06853
4.	,,	·3662			·07541	
Mean (of 4 measures)					·07903	
By capillary tubes (Quincke)					·07636	

(The mean of $K-k$ used to calculate $\frac{1}{b}$ was ·37485.)

Air-bubbles in Distilled Water.

D=1. Temp. 25° C.

No.	L.	K−k.	$\frac{1}{3 \cdot 282\ L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.	
1.	·9	·4112	·3385	·3104	·08455	·08263	Rejected.
2.	1·38	·4069	·2208	·0723	·08280	·07386	
3.	1·05	·3972	·2902	·1989	·07905	·07355	
4.	1·095	·4043	·2783	·1736	·08170	·07535	
5.	1·00	·4011	·3047	·2310	·08040	·07595	
6.	1·04	·4225	·2930	·2049	·08920	·08307	
7.	1·535	·4000	·1985	·0443	·08000	·07122	
Mean (of 7)					·08253	·07550	
By capillary tubes (Quincke)						·07235 at temp. 16°·2.	
If we reject also Nos. (3), (5), and (6) on account of the largeness of the fraction $\frac{a}{L}$, the mean result is...						·07348	
The exps. of M. Wolf (see Terquem's *Capillarité*, p. 34) give						·07345 at temp. 25° C.	

Air-bubbles in Bisulphide of Carbon.

D=1·2687. Temp. 25° C.

No.	L.	K−k.	$\frac{1}{3 \cdot 282\ L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
1.	1·25	·2180	·2438	·0093	·03015	·027351
2.	1·35	·2230	·2226	·0046	·03157	·0287
3	1·75	·2399	·1741	0	·03651	·03369
Mean					·03274	·0299
By capillary tubes (temp. 18°) (Quincke) ...					......	·03343

Air-bubbles in Olive-oil.

D = ·9136. Temp. 25°·8 C.

No.	L.	K−k.	$\frac{1}{3\cdot282\ L}$	$\frac{1}{b}$	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
1.	1·5	·3001	·2031	·0095	·04113	·03678
2.	1·7	·2858	·1792	·00377	·03735	·03387
3.	1·7	·2885	„	„	·03804	·03453
4.	1·56	·2905	·1953	·00719	·03850	·03470
5.	1·56	·2814	„	„	·03617	·03271
6.	1·485	·2751	·2052	·01041	·03457	·03122
7.	1·485	·2861	„	„	·03741	·03364
Mean					·03760	·03392
By capillary tubes (temp. 22°) (Quincke)					......	·03271

Air-bubbles in Oil of Turpentine.

D = ·8867. Temp. 25°·1 C.

No.	L.	K−k.	$\frac{1}{3\cdot282\ L}$	$\frac{1}{b}$	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
3.	1·34	·2665	·2274	·01199	·03149	·02818
4.	„	·2659			·03134	
Mean (of 8 measures)					·03033	·02818
By capillary tubes (temp. 21°·7) (Quincke)					......	·02765

(The mean value of K − k used in the calculation of $\frac{1}{b}$ is ·2615 cm.)

Air-bubbles in Petroleum.

D=0·7977. Temp. 24°·2 C.

No.	L.	K−k.	$\frac{1}{3\cdot282\,L}$	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
1.	1·475	·2838	·2066	·01033	·03212	·02890
2.	1·5	·2860	·2031	·0090	·03260	·02934
3.	„	·2858				
Mean (of 3 measures)					·03244	·02912
By capillary tubes (temp. 22°·3)					......	·02566

Air-bubbles in Absolute Alcohol.

D=·7906. Temp. 25°·3 C.

No.	L.	K−k.	$\frac{1}{3\cdot282\,L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
1.	1·57	·2532	·1959	·00326	·02533	·02335
2.	„	·2560			·02591	
3.	1·415	·2611	·2153	·0074	·02695	·02417
4.	„	·2548			·02566	
5.	1·41	·2539	„	„	·02548	·02324
6.	„	·2560			·02590	
7.	1·44	·2573	·2116	·0063	·02616	·02383
8.	„	·2591			·02655	
					·02599	·02367
By capillary tubes at 21°·8 (Quincke)					......	·02237
„ „ „ „ 15° (Mendeljeff)					......	·02365

Mercury in Air.
$D = 13{\cdot}5432$. Temp. 20° C.

No.	L.	K−k.	$\frac{1}{3{\cdot}282\ L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
6.	1·625	·2839	·1875	·00534	·5456	·4946
7.	1·7	·2861	·1792	·00377	·5546	·5037
8.	1·65	·2822	(C calculated by proportional parts.)		·5624	·5102
				Mean of 8 measures ...	·5503	·5028

(The mean of K−k used to calculate $\frac{1}{b}$ was ·2863.)

Bisulphide of Carbon in Water.
$D = 1{\cdot}2687 - 1$.

No.	L.	K−k.	$\frac{1}{3{\cdot}282\ L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
1.	1·275	·5510	·2389	·2082	·04069	·03872
2.	„	·5478			·04021	
3.	„	·5390			·03893	
4.	1·355	·5830	·2249	·1753	·04555	·04301
5.	„	·5808			·04520	
				Mean of 6 measures ...	·04256	·04086

(The mean of K−k used to calculate $\frac{1}{b}$ was ·5583.)

Chloroform in Water.
$D = 0{\cdot}4878$.

No.	L.	K−k.	$\frac{1}{3{\cdot}282\ L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
4.	1·8	·3450	·1693	·0089	·02902	·026296
5.	„	·3472			·02941	
				Mean of 5 measures ...	·03010	

(The mean of K−k used to calculate $\frac{1}{b}$ was ·35076.)

Olive-oil in Water.
D=1−0·9136.

No.	L.	K−k.	$\frac{1}{3\cdot282\ \mathrm{L}}$.	$\frac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
6.	2·37	·6941	·1286	·04185	·02082	·01818
7.	„	·6785			·01988	
				Mean of 7 measures ...	·02096	

(The mean of K−k used to calculate $\frac{1}{b}$ was ·69648.)

Turpentine in Water.
D=1−0·8867.

No.	L.	K−k.	$\frac{1}{3\cdot282\ \mathrm{L}}$.	$\frac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
9.	1·15	·4610	·2649	·1915	·01200	·01127
				Mean of 9 measures ...	·01177	

(The mean of K−k used to calculate $\frac{1}{b}$ was ·4562.)

Mercury in Aqueous Solution of Hyposulphite of Soda.
D=13·543−1·1248.

No.	L.	K−k.	$\frac{1}{3\cdot282\ \mathrm{L}}$.	$\frac{1}{b}$.	Grams per cm.	
					S. tension (Quincke).	S. tension, corrected.
	cm.	cm.				
4.	1·365	·2836	·2232	·01405	·4994	·4208
5.	„	·2730			·4628	
6.	„	·2680			·4459	
				Mean of 6 measures ...	·45107	

(The mean of K−k used to calculate $\frac{1}{b}$ was ·2749.)

Mercury in Water.

$D = 13{\cdot}543 - 1.$

No.	L.	K−k.	$\frac{1}{3{\cdot}282\ L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
3.	1·5	·2560	·20313	·00514	·4110	·3844
4.	„	·2605			·4256	
5.	„	·2607			·4262	
7.	„	·2527			·4005	
				Mean of 7 measures ...	·4258	

(The mean of $K - k$ used to calculate $\frac{1}{b}$ was ·26.)

Mercury in Olive-oil.

$D = 13{\cdot}543 - 0{\cdot}9136.$

No.	L.	K−k.	$\frac{1}{3{\cdot}282\ L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
3.	1·45	·2362	·21014	·00306	·3523	·31066
4.	„	·2282			·3288	
				Mean of 6 measures ...	·3419	

(The mean of $K - k$ used to calculate $\frac{1}{b}$ was ·2322.)

Mercury in Oil of Turpentine.

$$D = 13{\cdot}543 - 0{\cdot}8867.$$

No.	L.	K−k.	$\frac{1}{3{\cdot}282\,L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
1.	1·5	·1967	·20313	·0007	·2449	·2415
2.	,,	·2054			·2669	
3.	,,	·2044			·2642	
4.	1·815	·1970	·20313	0	·2456	·2304
				Mean ...	·2554	·236

(The mean of K−k used to calculate $\frac{1}{b}$ was ·2009.)

Mercury in Petroleum.

$$D = 13{\cdot}543 - 0{\cdot}7977.$$

No.	L.	K−k.	$\frac{1}{3{\cdot}282\,L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
3.	1·9	·2010	·1604	0	·2574	·23896
4.	,,	·1985			·2511	
5.	1·5	·2220	·20313	·0022	·3142	·29171
6.	,,	·2247			·3218	
				Mean ...	·2861	·2653

(The mean of K−k used to calculate $\frac{1}{b}$ was ·21155.)

Mercury in Alcohol.

$D = 13{\cdot}543 - 0{\cdot}7906.$

No.	L.	K−k.	$\frac{1}{3{\cdot}282\,L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
	cm.	cm.				
1.	1·5	·2443	·20313	·0037	·3805	·3569
2.	,,	·2574			·4224	
3.	,,	·2422			·3740	
				Mean of 6 measures ...	·4025	

(The mean of K − k used to calculate $\frac{1}{b}$ was ·248.)

Olive-oil in Alcohol.

$D = {\cdot}9136 - {\cdot}7906.$

No.	L.	K−k.	$\frac{1}{3{\cdot}282\,L}$.	$\frac{1}{b}$.	Grams per cm. S. tension (Quincke).	Grams per cm. S. tension, corrected.
3.	1·405	·1975	·21686	0	·00240	·00210
4.	,,	·1872			·00215	
				Mean of 4 measures...	... .. ·00226	

(The mean of K − k used to calculate $\frac{1}{b}$ was ·1917.)

The corrected results with hyposulphite of soda, bisulphide of carbon, and petroleum do not agree satisfactorily with the measures made with capillary tubes.

The general effect of the correction is to reduce the results by about 10 per cent., but in some cases, especially of drops of one liquid in another, the value of L is so small that the accuracy of the correction may be questioned. I hope soon to be able to lay before the Society fresh determinations of the surface-tension in these cases. When L reaches or approaches 2 centims. the term $\frac{1}{b}$ is generally insignificant, though the corrective factor C, which now reduces to $\frac{1}{3{\cdot}282\,L}$,

is still important. In fact a drop or bubble may be considered flat before the radius can be regarded as indefinitely great.

In those cases where the corrected value still exceeds the mean value obtained by the method of capillary tubes, the difference which was previously considerable is now for the most part insignificant; witness water, olive-oil, turpentine, and alcohol. It must also be remarked that the measures of flat drops or bubbles agree among themselves far less satisfactorily than the measures of capillary elevations. Thus the numbers quoted as obtained with capillary tubes are themselves the mean of several observations, not differing from each other as a rule by more than 2 per cent., though made with tubes of various diameters; while the observations of flat drops or bubbles differ often by as much as 15 per cent., or even more.

This very variation is indeed a matter of interest, and not easily accounted for*. For though M. van der Mensbrugghe has well pointed out † that the bubble when first blown must exhibit a higher surface-tension, owing to the absorption of heat from, and consequent lowering of temperature of, the surface-layers, yet it is not easy to believe that this deviation from the normal value would be of long persistence; nor indeed do Prof. Quincke's measures always show a diminution of tension with the time.

I think, however, that we may draw the conclusion that the method of capillary tubes, when care is taken thoroughly to wet the walls above the meniscus, leads to values which are not discredited, as we had been led to think, by the results of the method of flat drops or bubbles. This is a satisfactory conclusion to come to, since the method of elevation in capillary tubes is that which has been most frequently employed for measuring the surface-tension. Prof. Quincke's value

* Mr. Bashforth (see 'An Attempt to test the Theories of Capillary Action,' p. 10) remarks on the difficulty of making any accurate direct measurement of the height $K-k$, and Prof. Guthrie has somewhere noticed the same difficulty. But Prof. Quincke's measures of $K-k$ do not show a percentage-variation much greater than that of the quantity $K\sqrt{\frac{1}{2}}$, in determining which the same difficulties do not occur.

† "Etudes sur les variations d'énergie potentielle des surfaces liquides," *Mém. de l'Acad. de Belgique*, t. xliii. 1878.

(·0825 gr. = 81 C.G.S. units) of the surface-tension of water has been employed by Lord Rayleigh * to calculate the wave-length in an oscillating water-jet, and leads, as he himself points out, to too low a result. Had he made use of the corrected value (T = ·0735 gr. = 72·1 C.G.S. units), the results of p. 82, *loc. cit.*, would have been in very close agreement with theory.

In conclusion, I would remark that the great value of this particular paper of Prof. Quincke's does not, as it seems to me, depend so much on the absolute accuracy of the results presented as on the emphasis with which, at the time it was written, it represented the capillary constant to be measured as a surface-tension, and on the justice of the general considerations which are put forward, and which remain unimpeached.

A. M. Worthington.

Clifton, Bristol, June 2, 1885.

P.S. For the benefit of readers of Maxwell's 'Theory of Heat,' in which Prof. Quincke's results are given in a synoptic table, I here reproduce the table with the corrected values. Those in brackets I have been unable to check. It must be borne in mind that the numbers in the second column of tensions are still somewhat uncertain.

The values are given in grammes weight per linear metre.

Superficial Tensions at about 20° C.

Liquid.	Specific gravity.	Tension separating the liquid from		
		Air.	Water.	Mercury.
Water	1·0	7·35	0	38·44
Mercury	13·543	50·28	38·44	0
Bisulphide of Carbon	1·2687	2·99	4·09	[37·97]
Chloroform	1·4878	[3·12]	2·63	[40·71]
Alcohol	0·7906	[2·36]	...	35·69
Olive-oil	0·9136	3·39	1·82	31·07
Turpentine	0·8867	2·82	1·13	23·60
Petroleum	0·7977	2·91	[2·83]	26·53
Hydrochloric acid	1·1	[7·15]	...	[38·41]
Solution of Hyposulphite of Soda	1·1248	6·85	...	42·08

* "On the Capillary Phenomena of Jets," Proc. Roy. Soc. no. 196 (1879).

XXI. *On the Use of Daniell's Cell as a Standard of Electromotive Force.* By J. A. Fleming, *M.A., D.Sc. (Lond.), Fellow of St. John's College, Cambridge, Professor of Electrical Technology in University College, London*.*

[Plate I.]

The extensive use now being made of strong currents of electricity for purposes of illumination necessitates the employment of instruments for measuring current-strength and electromotive force of high values. The employment of electricity for telegraphic purposes, and especially in submarine telegraphy, compelled attention to a common accuracy in measurement of resistance and capacity; but for these purposes the measurements of electromotive force and currents are not of such importance as they are in the recent developments. This requirement has drawn the attention of electromechanicians to the subject, and led to the introduction of numerous forms of electromotive force and current-indicators, variously called potential galvanometers, voltmeters, pressure-gauges, ampere- or am-meters.

Considering first the voltmeters, they may be classified, according to Sir W. Thomson's nomenclature, into two classes —idiostatic and heterostatic. In the second class the magnetic force at a point in the neighbourhood of a conductor conveying a current is compared with another magnetic field either of the earth or of a permanent magnet, and the difference of potential at the ends of the conductor deduced therefrom. In the first class no magnetic field is made use of other than that created by the current itself.

In the case of heterostatic instruments the readings require to be controlled by a special determination of the value of the auxiliary field; and in the case of an ordinary tangent- or sine-galvanometer, the determination of the earth's horizontal magnetic force is a task requiring great care and considerable precautions. In the idiostatic instruments, in many cases, springs are used to obtain a force with which to compare the magnetic force in the neighbourhood of a conductor. The elasticity of these springs is not necessarily permanent, and is

* Read June 27, 1885.

liable to change by temperature as well as time. Accordingly in these instruments also, the constant must from time to time be determined. Pending the appearance of the new instruments promised by Sir W. Thomson, in which no springs nor permanent magnets are used, it is necessary to fall back upon galvanic cells to establish a standard of electromotive force, and the present paper is a brief collection of facts concerning the use of Daniell's cell for this purpose, and its application in the measurement of currents of various strengths. In all the experiments and methods cited below the cell has been used only to create a difference of potential, and not allowed to send any but a very small current, the means employed for comparisons being a slight modification of Clark's potentiometer, as shown in fig. 1 (Plate I.). On a stout mahogany board are fastened down two boxwood scales, each 5 feet long, divided into inches and tenths; these scales are fixed about $\frac{1}{4}$ inch apart and parallel, so as to form a groove between them. On these scales are stretched two fine uniform German-silver wires A B, A′ B′, about ·013 inch in diameter, and having a resistance of about 1 ohm to the foot-run: one end of both wires is soldered to a thick copper junction-piece J, and the other ends respectively to copper pieces connected to terminals M, M′. The wire thus forms one length of about 10 feet stretched over two scales. This forms the potentiometer wire; its length is divided by the scale into 1200 parts, and each tenth of an inch can be divided by the eye into 10, making a possible division of 12,000. To the terminals M, M′ are connected five or six large-gravity Daniell cells, and the poles of this battery are short-circuited by an Edison 16-candle lamp of 240 ohms cold resistance. This enables the battery to keep a more constant difference of potential between the terminals M, M′.

A very constant E.M.F. can be obtained by using small accumulator-cells in series: the poles being joined by a carbon-filament lamp, and the leads to the terminals M, M′ taken off from the opposite sides of the lamp.

It is easy to calculate what number of cells are required to maintain a given difference of potential, say 2 volts, at the extremities of the potentiometer-wire. For let n be the

number of cells, e the E.M.F. of each, and r the internal resistance, and let R be the resistance of the lamp and potentiometer-wire combined, and v the required difference of potential desired at the terminals M, M′; then

$$v = \frac{ne\mathrm{R}}{nr + \mathrm{R}},$$

which determines n. If r is not known, it can be determined by a second experiment, in which v is observed in the case of a given number of cells.

The current along this German-silver wire makes a fall in potential at about the rate of 1 volt in 5 feet. On one side of the board is fastened a broad copper strap $b\,b$, having six terminals fastened upon it. Between the last of these terminals and the end of the scale-wire A′ is inserted a reflecting-galvanometer of 5000 ohms resistance, and an additional resistance of 50,000 ohms R.

To the other terminals s, s on this copper strip are connected one pole (like to the pole of the battery B connected to M′) of each of the cells c, c' to be compared; and the other poles of these cells are connected with sliders S, S′ travelling over the wires. These sliders are blocks of wood sliding in the groove between the scales, and overhanging the wires. On them are German-silver spring-strips as shown in the figure, and which, when pressed down, make contact with the wire. The strips are backed with leather to avoid the production of thermoelectric currents. By using two or more of these sliders, it is easily seen that several cells may be balanced at once on the potentiometer; and in particular two cells c and c' can be compared in respect of electromotive force very accurately, even although the E.M.F. of the main battery is not quite constant. The introduction of the resistance R prevents any but the very smallest currents passing in the cells when the place of balance is being found on the potentiometer. The German-silver strips g, g on the sliders make contact only when pressed down; so that in the normal condition the cells c, c' are insulated. With the galvanometer in a sensitive condition it is very easy to read a difference of $\frac{1}{10000}$ of a volt on the wire, and $\frac{1}{1000}$ can be read with great accuracy.

Electromotive forces are read off directly as lengths, since the E.M.F. of the cells c, c' is directly as the distance of the constant points of their respective sliders from the end A′ of the wire. Great care has to be taken in the first instance to stretch the wire uniformly, and to calibrate it if it presents any want of uniformity of resistance. Provided with this convenient means of directly comparing electromotive forces, attention was next directed to a modification of Daniell's cell suitable for the experiments required. In Dr. Alder Wright's extensive researches on the subject*, the form of cell employed was that sometimes called Raoult's form, in which two small beakers contain the two solutions, and are connected by an inverted Y-tube, the ends of which are tied over with thin bladder. This form of cell is undoubtedly convenient for some purposes, but not for others, as when the cell has to be heated or cooled for comparison at different temperatures. Moreover, the siphon becomes filled in a very short time with a mixture of solutions by diffusion; and if the levels of the liquids are not exactly equal, a siphoning action is added to that of diffusion in carrying liquid over from one side to the other. After some numerous trials of all existing forms which have been proposed for Daniell's cell, the following was devised, which, though more bulky than others, has yet given great satisfaction, and has the great recommendation of always standing ready for use.

A large U-tube, about ¾ inch diameter and 8 inches long in the limb, has four side tubes (see Pl. V. fig. 2). The two top ones, A and B, lead to two reservoirs Z and C, and the bottom ones C and D are drainage-tubes. These side tubes are closed by glass taps. The whole is mounted on a vertical board, with a pair of test-tubes between the limbs. Suppose, now, a Daniell's cell is to be formed with solutions of zinc sulphate and copper sulphate, and that the zinc-sulphate solution is the denser. The left-hand reservoir S Z is filled with the zinc solution, and the right-hand reservoir S C with the copper solution.

* "On the Determination of Chemical Affinity in Terms of Electromotive Force.—Part V. On the Relationships between the Electromotive Force of a Daniell Cell and the Chemical Affinities involved in its Action." Proceedings of the Physical Society of London, Vol. V. Part I. p. 44 *et seq.* [Phil. Mag. vol. xiii. p. 265.]

The electrodes are zinc and copper rods, Zn and Cu, passed through vulcanized-rubber corks, P and Q, fitting air-tight into the ends of the U-tube.

The operation of filling is as follows:—Open the tap A and fill the whole U-tube with the denser zinc-sulphate solution; then insert the zinc rod and fit it tightly by the rubber cork P. Now, on opening the tap C the level of the liquid will begin to fall in the right-hand limb but be retained in the closed one. As the level commences to sink in the right-hand limb, by opening the tap B copper-sulphate solution can be allowed to flow in gently to replace it; and this operation can be so conducted that the level of demarcation of the two liquids remains quite sharp, and gradually sinks to the level of the tap C. When this is the case, all taps are closed and the copper rod inserted in the right-hand limb.

Now it is impossible to stop diffusion from gradually mixing the liquids at the surface of contact; but whenever the surface of contact ceases to be sharply defined, the mixed liquid at the level of the tap C can be drawn off, and fresh solutions supplied from the reservoirs above.

In this way it is possible to maintain the solution pure and unmixed round the two electrodes with very little trouble; and the electrodes, when not in use, can be kept in the idle cells or test-tubes L and M, each in its own solution. In making experiments concerning temperature, the whole U-tube can be immersed in a vessel of water or ice up to nearly the top of the reservoirs, and the temperature in the solutions taken by means of a thermometer passing through the rubber-cork. Each of the electrodes can be removed for examination or change without in the least disturbing the surface of contact of the solutions. If experiments are being made in which the sulphate-of-copper solution is the denser, the position of the solutions is interchanged. The bottle R serves to collect the waste solutions.

The electrodes are made of rods of the purest zinc and copper, about 4 inches long and $\frac{1}{4}$ inch diameter. The zinc found most suitable is made from zinc twice distilled and cast into rods; the copper prepared by electro-depositing on a very fine copper wire, until a cylinder of the required thickness is obtained.

With these appliances to hand, all the facts recorded by previous experimenters have been carefully repeated and confirmed, and the influence of each variable upon the electromotive force examined. The results are collected as follows. For the sake of brevity, a Daniell's cell in which zinc, sulphate of zinc, sulphate of copper, and copper are the elements will be called a normal Daniell; and the statements here below refer to the variations in the difference of potential between the poles of the normal Daniell, when sending either no current or only an infinitesimal one, caused by variations in the physical state of the four elements. In each set of experiments the greatest care was taken to keep all the elements constant, except the one which was purposely being varied in order to detect the influence of it on the whole electromotive force.

1. *The Effect of Variation in the Copper Surface and Condition.*

In these experiments the copper- and zinc-sulphate solutions were sometimes of the same specific gravity, sometimes different; and in some cases the zinc electrode was a rod of the purest cast zinc amalgamated with pure mercury, sometimes a rod of commercial zinc wire cleaned but not amalgamated. Some scores of observations were made with identical zinc plate and solutions, but various kinds of copper plates*; and all observations have confirmed the conclusions of Dr. Alder Wright that the most uniform results are obtained from

* All the following values are given in real volts, taking Lord Rayleigh's value for the mean B.A. unit of resistance as equal to ·9867 earth-quadrant per second.

The determinations have been made against a Clark cell, kindly compared by Lord Rayleigh with his No. 1 cell, whose value is given in his paper in the Phil. Trans. part ii. (1884) as 1·435 true volt at 15° C. My standard, called hereafter F_{20}, is greater than this by 3 parts in 4940, or is 1·436 volt at 15° C.; and experiments have shown that its variation-coefficient is nearly that found by Lord Rayleigh, viz. ·082 per cent. per degree diminution of E.M.F.

Accordingly, the value of this standard Clark cell F_{20} has been taken as equal to

$$1{\cdot}436(1-{\cdot}00082\,t^{\circ})\text{ volt at } t\,\text{C.},$$

and all values given in the text are in terms of this.

copper plates freshly electrotyped over with a new clean pinkish surface of virgin copper, when the plate is taken straight out of the electrotyping bath and put into the cell without any delay or touching except a slight rinse with distilled water. The result of comparing a freshly electrotyped rod with a rod scraped and glass-papered, was to show that the scraped copper rod gave a higher electromotive force by about 4 parts in 629, or 6 parts in 1000. When both rods were freshly electrotyped in the same bath, and inserted in the same cell, there was absolutely no difference between them. Cells were compared with solutions of equal density 1·2 at 15° C. and amalgamated pure cast zinc, but different copper rods, as follows :—

	E.M.F.
Electrotyped copper rod . .	1·105 volt.
Scraped copper rod	1·111 „

The exact amount of difference varied slightly in other experiments ; but with equally clean surfaces, the electrotyped fresh surface has a lower electromotive force than the scraped. The effect of amalgamating the copper rod is, like electrotyping, to lower its value below that of the clean scraped, but it is not so uniform. The following are values obtained from equal copper rods in the same cell, one having an electroplated surface and the other being slightly amalgamated with pure mercury :—

Freshly electro-deposited copper rod.	Freshly amalgamated copper rod.
1·103	1·104
1·106	1·104
1·105	1·104
1·106	1·105

The mean of the values of the electro-deposited copper exceeds by about 1 in 1000 the mean of the amalgamated copper ; but if the amalgamation is done thickly it causes more serious deviations, and though more convenient is not quite so reliable as electroplating the rod with fresh copper, but is preferable to employing simply a scraped or glass-papered surface of rolled copper. A large series of determinations were next made on the effect of oxidation of the copper

surface. If a copper rod, newly electroplated, is left in the copper-sulphate solution, it gradually gets oxidized and covered with brown patches of oxide, and if amalgamated, the mercury sinks in and the surface gets brown and patchy. When this is the case the electromotive force rises, and by uncertain amounts, depending on the degree of oxidation. It is very remarkable how small a trace of brownish oxidation on the surface raises the electromotive force several parts in 1000, amounting in some cases to nearly 1 per cent. The following is one set out of many experiments on this point:—

Two solutions of zinc and copper sulphate were prepared of the pure crystals. The specific gravity of the zinc sulphate was 1·4, and that of the copper sulphate was 1·1. A rod of pure unamalgamated zinc and one of electrotyped copper was also taken. Keeping all other conditions constant, the rod of copper was first cleanly and carefully electrotyped over with a new fresh surface of copper, and exhibited no trace of oxidation; and the E.M.F. of this cell was then taken against a carefully tested standard Clark cell of known value; and the rod was then suffered to oxidize on the surface by successive exposure to the air, the E.M.F. of the cell being taken at each stage.

	E.M.F. of cell.
Copper, perfectly pure, unoxidized . .	1·072 volt.
" slightly oxidized, brown spots.	1·076 "
" more oxidized	1·082 "
" covered with dark-brown oxide film	1·089 "
" cleaned, replated with fresh pinkish electro-surface . .	1·072 "

Many other experiments of this sort showed the same thing. A Raoult cell was formed by taking two beakers, one containing zinc sulphate of specific gravity 1·2, and the other copper sulphate of the same specific gravity, and using amalgamated cast zinc and electro-deposited copper rods. The beakers were connected, when required, by a piece of clean cotton-wick dipped in water, and connecting both solutions by dipping into each. The copper pole was first freshly electroplated, and the following values obtained for the E.M.F. of the cell as it gradually oxidized:—

	E.M.F. of cell.
Freshly electro-deposited surface of copper	1·105 volt.
Slightly oxidized, faint brown tinge . . .	1·106 „
More oxidized	1·107 „
Still more oxidized	1·109 „
Re-electroplated surface	1·105 „

Hence these and many similar experiments all teach that oxidization, even the slightest trace, of the copper raises the E.M.F.; and that, in order to get the real value proper to the combination, the copper must be electrotyped over with a thin pure film of copper, and exhibit no trace of brown spots of oxide, and be used at once.

2. *The Effect of Variation in the Zinc Surface and Condition.*

Numerous experiments have been made to investigate whether there is any certain difference between zinc amalgamated or unamalgamated or cast or rolled. There is very little, if any, certain difference between perfectly pure cast zinc unamalgamated and the same amalgamated with pure mercury. There are greater differences if the zinc is not pure, and variations are introduced if impure mercury is used for amalgamation, all of them uncertain in amount.

The effect of oxidation of the zinc is to lower the electromotive force. If the bright surface of the zinc becomes tarnished, it always shows a slightly lower E.M.F. The smallest deposit of copper upon the zinc, due to diffusion of the copper salt into the zinc, is indicated by a marked depression, amounting to 2 or 3 per cent. On the whole, the only consistent values are obtained from chemically pure zinc with a bright fresh untarnished surface, whether amalgamated or not; and the best results are given with pure zinc amalgamated with pure mercury. In Dr. Alder Wright's memoir the above conclusions are enforced by tabulated results of most extensive experiments.

On the question of amalgamation of the zinc we may quote a note on the subject by M. G. Lippmann in the *Journal de Physique.* There is an opinion expressed by some authors that amalgamated zinc has a higher E.M.F. than unamalgamated, even if pure. If a plate of each of the two substances

be immersed in sulphate-of-zinc solution, a couple is formed in which amalgamated zinc forms the negative pole, inasmuch as it is the more readily acted upon by oxygen. Such, at least, is the result obtained if ordinary commercial zinc is used and ordinary sulphate-of-zinc solution. In a recent work, M. W. Robb shows that if care be taken to use electro-deposited zinc, and also zinc-sulphate solutions deprived of free acid, the element zinc, zinc sulphate, and amalgamated zinc will not manifest any appreciable E.M.F. The superiority of amalgamated zinc over ordinary zinc is easily explained; but when pure zinc is used, deprived of any oxide on the surface by slight rinsing in dilute sulphuric acid before placing it in the sulphate of zinc, there is little or no certain difference, to the extent of 1 part in 1000 in the case of the normal Daniell, between the pure zinc amalgamated or unamalgamated.

3. *The Influence of Density of the Solutions on the Electromotive Force.*

The chief reason for the differences in the values assigned by various observers to the E.M.F. of the normal Daniell is due to the great influence that the specific gravity of the two exciting solutions exerts on the resultant E.M.F. of the combination; and the general law of the effect is this—If a Daniell cell be formed of amalgamated pure zinc, freshly-electrotyped copper, and solutions of pure zinc sulphate and copper sulphate of equal specific gravity, then, taking this cell as a standard of reference, increasing the density of the zinc sulphate lowers the electromotive force, and increasing the density of the copper sulphate raises the electromotive force, within, at any rate, the limits of density from 1·01 as an inferior, up to saturation as a superior limit. Zinc sulphate saturated at 15° C. has a density of a little above 1·4, and copper sulphate similarly saturated 1·2; and Dr. Alder Wright shows by experiments that the increment and decrement of E.M.F. for identical increment or decrement of density of both solutions are so nearly equal that for equally dense solutions, within limits, the E.M.F. is independent of the absolute density of both. This fact has been confirmed by many other observers. Amongst other careful experiments may be noticed

those of Carhart *, whose experiments were specially directed towards ascertaining the influence which variation in the density of the zinc sulphate exerts on the resultant E.M.F.

In using a Daniell cell as a laboratory standard it is necessary, therefore, to prepare and standardize the solutions of zinc and copper sulphates with the same care as if they were to be used for volumetric analysis. It is a good plan to prepare two large stock bottles of solutions, and having carefully determined the density to adjust them to known specific gravity by the aid of the specific-gravity bottle or hydrometer. For general use two standard solutions of each salt are specially useful. First, a solution of sulphate of copper very nearly saturated at 15° C. and having a specific gravity of 1·200, and a solution of sulphate of zinc of equal density. Secondly, a solution of sulphate of copper of density 1·100 at 15°, and a solution of sulphate of zinc of 1·4. These last values are chosen because they were employed by Sir W. Thomson in his standard gravity-cell; and they can be used in either his form of gravity-cell, or in the U-tube form above, or in Raoult's form of separate vessels and siphon †.

A very large number of comparisons have been made of the E.M.F. of cells set up with these solutions and the E.M.F. of Clark's cells, whose value has been compared directly with cells standardized in absolute measure.

If a Daniell cell is carefully made up, either in the Raoult form or U-tube form, of solutions of pure zinc and copper sulphate not sensibly interdiffused at the level of contact, and with pure amalgamated cast zinc and freshly electrotyped copper plate, which is evenly plated with a new uniform pinkish deposit of electro-copper free from all brown spots of oxide, the E.M.F. of this cell, taken at once, is very close to 1·102 true volt, and the ratio of the E.M.F. of this cell to a cor-

* A paper read before the American Association for the Advancement of Science, Sept. 5, 1884. See 'Telegraphic Journal and Electrical Review,' vol. xv. p. 250.

† If 28·25 parts by weight of pure crystallized sulphate of copper ($CuSO_4$, $5OH_2$) are dissolved in 71·75 parts by weight of distilled water, the resulting solution will have very nearly a specific gravity of 1·200 at 18° C.; and if 16·5 parts of the crystals are dissolved in 83·5 parts of water, the solution will have a density of 1·100 at 15° C.

For the zinc-sulphate solutions take 55·5 parts by weight of crystallized

rected Clark cell at 15° C. is very nearly ·768 to unity *; the Clark cell being taken as 1·435 at 15° C.

If, instead of taking the equidense solutions, we take zinc sulphate of specific gravity 1·400 and copper sulphate of 1·100 at 15° C., and the same plates, the E.M.F. of the cell lies close to 1·072 volt, and the ratio of the E.M.F. to that of the corrected Clark is ·747.

If, however, instead of taking the electromotive force at once after the freshly electroplated copper pole is introduced into the cell, the cell is allowed to stand an hour or so, both the above values will be increased by about ·003 volt, provided always that no interdiffusion of solutions has taken place, and that the zinc retains a perfectly bright untarnished surface.

4. *Influence of Temperature on the Electromotive Force of the Normal Daniell Cell.*

The researches of experimenters who have studied the Clark cell have established the fact that its E.M.F. diminishes with rise of temperature. The exact value of the coefficient of variation seems to depend on the mode in which the cell is made up; and very careful examination has been made of the Daniell cell as above described, to see if its real E.M.F. is affected by temperature. Some writers have asserted that it is; but it is obvious that the variation of internal resistance must be eliminated entirely by the use of a null method of observation of the E.M.F. The condenser method is not a sufficiently accurate one to apply, and the potentiometer method is the most trustworthy.

Two U-tube cells were prepared with 1·4 sp. gr. zinc sulphate and 1·1 sp. gr. copper sulphate; and these cells were respectively immersed, the one in a water-bath at 20° C. and the other in melting ice at 0°. A pair of zinc and copper

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zinc sulphate ($ZnSO_4$, $7OH_2$) and dissolve in 44·5 parts of distilled water. The resulting solution will have at 20°·5 C. a specific gravity of 1·400.

If 32 parts by weight of the crystals are dissolved in 68 of water at the same temperature, the solution will have a density of 1·200. These are useful densities.

* Lord Rayleigh assigns a value very close to ·770 for this ratio, and Dr. Alder Wright ·765. The figure in the text is derived from about 50 experiments of my own.

poles was likewise prepared; and when the solutions in the U-tubes had acquired the temperature of the baths, the E.M.F. of each cell was taken with the pair of zinc and copper plates, first in one and then in the other, with the following results:—

Plates in the warm cell at 20° C. E.M.F. of cell.	Plates in the cold cell at 0° C. E.M.F. of cell.
1·081	1·082
1·079	1·082
1·079	1·082
1·078	1·083

The experiments showed a very small but decided fall of E.M.F. as the cell is warmed, and at the rate of about 3 parts in 1000 for 20° C. This is only about $\frac{1}{50}$ of the variation of a Clark cell for the same range; and, practically, we may say that the E.M.F. of a Daniell cell is independent of temperature for such range as occurs in the natural temperature of the air in our climate *. This quality of the normal Daniell is very important, and goes very far towards helping it to sustain its position as a standard cell against its rival the Clark cell.

The various coefficients of temperature-change which have been found for Clark cells indicate that it is unsafe to rely upon any cell taken at random, whose history is unknown, having a coefficient of variation accurately the same as that of the cells whose coefficients have been actually determined.

It would be a great advantage if instrument-makers would construct these cells in the form suggested by Lord Rayleigh —enclosed in a test-tube and having gutta-percha-covered leading-in wires passing through a rubber stopper. The coefficients of variation would then be easily obtained for any cell, just as those of standard resistance-coils are ascertained and marked on each cell with the range of temperature over which it is applicable.

* The same result has been obtained by Mr. Preece in his experiments on the effects of temperature on the electromotive force and resistance of batteries, see 'Electrician,' March 3, 1883, vol. x. page 367. He gives a table showing the E.M.F. at various temperatures, obtained by the condenser method, and shows that there is no perceptible change in E.M.F. of a normal Daniell between 0° and 17°, and a slight fall subsequently of about 9 parts in 1000 between 17° and 28°, but a rise, however, after reaching 63°.

As a check on the foregoing experiments on the Daniell, the coefficient of variation of the standard Clark cell used was obtained. Two cells were taken, exactly equal at 18° C., and one of them was immersed for 48 hours in melting ice. The difference on the potentiometer-wire was then obtained between this cold cell and its fellow kept in water at 18° C. The potentiometer-readings were as follows :—

	i.	ii.	iii.
B, cell at 0° C. . . .	961	971	974·4
A, cell at 18° C. . . .	947	957	960
	14	14	14·4

From the experiment 1 the reading for the warm cell would have been $947+\frac{14}{6}=949\frac{1}{3}$ at 15° C. And hence the coefficient of variation is $\frac{14}{18}$ in $949\frac{1}{3}$, or ·0819 per cent. in the neighbourhood of 15° C. Lord Rayleigh gives ·082 as the value for his cells. It is obvious that Clark's cells cannot be used for standardizing galvanometers without a careful determination of their coefficients of variation.

The normal Daniell cell has a certain advantage in that when null methods for determining electromotive force are employed, its value is independent of temperature throughout a considerable range.

By the employment of the above two instruments—a potentiometer as described and a standard normal Daniell carefully constructed with all the precautions named—it is very easy to make very accurate measurements of strengths of currents of large magnitude. If a resistance is formed of such character that the current to be measured can be passed through it without much affecting its temperature, and the potential measured at the extremities of this resistance by means of a comparison on the potentiometer between it and that of the Daniell, this gives at once the current.

In order to construct a resistance whose value at the instant of passing the current can be accurately measured, the following device is adopted :—On a board are mounted a series of copper blocks *a*, *a*, *b*, *b*, like the connection-pieces on a resistance-box (see Pl. I. fig. 3). These can be connected by plugs *p*, *p*. At opposite sides and ends are main terminals as

M′; and the blocks a, b are connected by brass or German-silver wires wound in a spiral; similar coils of equal resistance connect each pair of opposite blocks. The number of coils must be an odd number.

If the plugs 1, 11, 3, 9, 5, 7 are put in, it is obvious all the coils R_1, R_2 . . . R_7 are a series, and their resistance can be measured: call it r. If, then, the other pegs are inserted, the coils are now in multiple arc or parallel, and if there are n coils the resistance is $\frac{r}{n^2}$. By this arrangement the resistance in parallel can be inferred from the resistance in series; and although each coil has a very small resistance, yet by using a large number, not only is a very easily measurable resistance obtained when the coils are in series, but a resistance of large current-carrying capacity when they are put in parallel.

The mode of using it is as follows:—The pegs are all put in, and the current to be measured is sent through the coils in parallel. By means of the potentiometer and standard-cell, the difference of potential is found between the terminals M and M′ when the current is passing. The alternate pegs are then removed, the current stopped, and the resistance taken of the coils in series, and the time noted which has elapsed between the measurement of potential and of the resistance. A few observations are taken of the resistance at intervals of time, by which to construct a curve of cooling; and by projecting back the curve, it is easy to ascertain very nearly the resistance at the time when the potential was measured. If small currents only are employed, it is not necessary to change the resistance; the current can be sent through it in series, and its resistance also measured in series. The writer has had constructed a large resistance of this kind at the Victoria Electric Lighting Station, for the measurement of dynamo currents up to 500 amperes. In this case the resistance consists of 36 wires of brass, No. 14 B.W.G., arranged in parallel, and of equal resistance. One of the wires can be disconnected and arranged instantly on a bridge to measure its resistance; and in this way, after measuring the potential at the ends of the 36 wires in parallel, with the current passing through them, one wire is disconnected, and its resistance taken immediately; from which observations it is possible to approximate very accurately to

the resistance of the whole wires in parallel. In order to afford data for constructing such resistances, experiments were made of passing various currents through coiled spirals of naked wires of different sizes and materials.

A large number of wires were prepared, of copper, brass, iron, German-silver, each 25 feet long, and of six sizes respectively, Nos. 10, 12, 14, 16, 18, 20, B.W.G., the diameters being given below. These wires were coiled into spirals round wooden rods about one inch diameter, and the turns of the wire well separated, so that each coil or spiral was about 18 inches long. Measured steady currents were sent through these for some hours, and so adjusted that after the temperature had become steady the wires were all at a temperature just about bearable by the hand, that is near 60° C. The currents respectively carried were as follows :—

Size of wire.	No. 10 B.W.G. ·134 inch diam.	12 ·109	14 ·083	16 ·065	18 ·049	20 ·035
Currents carried in Amperes.						
German Silver ...	18·75	13·5	8·25	6	4·12	3
Brass	30	18·75	15	9·75	7·5	5·25
Iron	18	11·25	10·5	8·25	5·25	3·75
Copper	49·5	38	26·25	20·25	15	9

These currents passed through the above-described naked spirals bring the respective wires to about a temperature of 60° C., when equilibrium is established; and for the purposes of measuring currents, not more than one third of the above currents should be used with wires of the size appended. Thus for 300 amperes, about 50 No. 10 B.W.G. wires will carry it without much sensible elevation of temperature; and by arranging 50 wires so that their resistance can be quickly measured in series, a resistance can be made suitable for measuring the potential at the ends of a known resistance.

By the use of this method it is easy to standardize any current or potential-galvanometer at any part of the scale, and

obtain the absolute or corrected value of the deflections; and these methods have been employed with success for some time in standardizing the working galvanometers used in the lamp factory of the Edison and Swan United Electric Light Company.

In conclusion may be given other results, collected from various authors, respecting the electromotive force of the Daniell cell.

Wiedemann (*Galvanismus*, vol. i. cap. iv., *Bestimmung der Electromotorischen Kraft*, p. 341) gives a description of Raoult's cell (see Raoult, *Ann. de Chim. et Phys.* [4] t. ii. p. 345, 1864), and states that Raoult finds that copper-foil has higher electromotive force than electro-deposited copper by about $\frac{1}{200}$; and attributes it to the oxides of copper contained in it. He also confirms the invariability of E.M.F. with temperature at least between 10° and 50°; and states that with pure amalgamated zinc and electro-deposited copper, solution of saturated sulphate of copper and solution of sulphate of zinc, containing 1 part of crystals to 1 part of water = 1·35 sp. gr. at 20°, the electromotive force is 1·124 electromagnetic units. This, corrected by the Cambridge value of the B.A. unit, is 1·109 volt.

Sir W. Thomson (p. 245 of 'Papers on Electricity and Magnetism') finds the electrostatic measurements of a Daniell cell to be ·00374. The nature of the solutions and electrodes are not given. Taking the value of v as 3×10^{10}, we have the E.M.F. as 1·12 B.A. volt, which, reduced to true volts, gives 1·105 volt.

Lord Rayleigh gives the ratio of a Daniell set up with amalgamated pure zinc, electro-deposited copper, and solutions of sulphate of zinc and copper, each of sp. gr. 1·1. Five observations of the ratio of this cell to that of a known Latimer-Clark cell at 16° C., taken as unity, gave ·7702, ·7710, ·7705, ·7698, ·7702, mean ·7703; and since the Clark is 1·435 volt, this gives the Daniell as 1·105 volt.

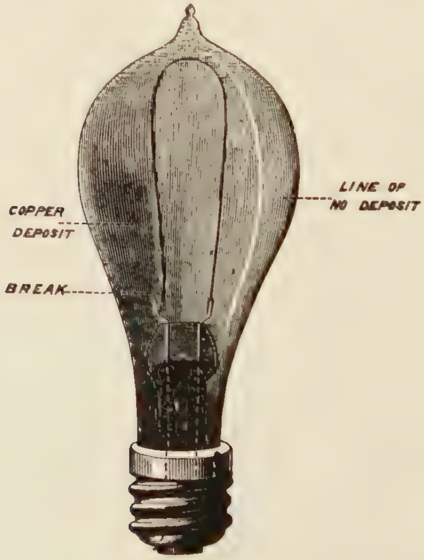
Latimer Clark (Journ. Soc. Tel. Eng., January 1873) gives it as 1·11, which, reduced to true volts, is 1·095; and Dr. Alder Wright (Proc. Phys. Soc. London, vol. vi. p. 292) gives the value of a normal Daniell set up with solutions of the same molecular strength, preferably of strength m M SO_4 100 OH_2,

where m is near 2—that is with copper sulphate nearly saturated, and zinc sulphate of equivalent molecular strength, and pure amalgamated zinc plates and electro-deposited copper—as 1·114 B.A. unit, or 1·099 true volt.

None of these are very far from the value assigned to the standard cell described above, viz. 1·102 volt, with equidense solutions and metals as described.

XXII. *On Molecular Shadows in Incandescence Lamps.* By J. A. Fleming, *M.A., D.Sc. (Lond.), Fellow of St. John's College, Cambridge, Professor of Electrical Technology in University College, London**.

Since presenting a short note on the above subject in 1883 many further opportunities have occurred for observing the conditions under which molecular shadows are formed in incandescence carbon-filament lamps, and of correcting one or



two statements then made. It has been observed in an immense number of cases, that not only do incandescence lamps become

* Read June 27, 1885.

coated on the interior of the glass with a deposit of carbon, but that the envelope may have deposited upon it a metallic film, derived from the leading-in wires to which the carbon filament is clamped. In the Edison lamp the platinum wire only just passes through the glass, and is connected with copper wires broadened out into a clamp ; the filament is gripped in these clamps and then electro-plated over with copper to effect a good junction. In the Swan lamp the platinum wires are joined directly on to the carbon. It occasionally happens that there is an unusual amount of resistance at the clamps, or that by excessive electromotive force more current is forced through the lamp and more heat generated everywhere. In this case the tendency will always be to increase and go on increasing the resistance, and, therefore, the temperature at the point of highest resistance. Suppose this occurs on the clamp or on the leading-in wire, then experience shows that the metal is volatilized and deposited as a film on the glass. This metallic deposit is not uniform ; it is thickest nearest the base of the lamp and gradually thins away up to the crown, and at a certain height is thin enough to transmit light. It is not very uncommon to obtain Edison lamps with this copper deposit. The colour of transparent copper is a fine sage green inclining to blue; compared with the colour of gold leaf seen by transmitted light, it very closely resembles it. On one occasion the writer obtained a lamp with a silvery metallic film deposited over it on the inside of the glass. From the outside it had a mirror-like lustre; on breaking the lamp this film was seen to be brownish and not brushed off by the finger, but it could be removed by scratching. It was not removed by holding in the oxidizing flame of a Bunsen burner: therefore it was not carbon. It was not removed by nitric acid; but on boiling a fragment of the glass, covered with this metallic deposit, in nitro-hydrochloric acid the film disappeared. It was therefore probably platinum. The film was transparent, permitting objects to be seen through it, and transmitted brownish light.

Now, under certain circumstances, a line of no deposit is formed on the surface in the plane of the filament, which is, as it were, the shadow of one side of the loop. This indicates that the process of molecular scattering, which is going on at

some spot on one or other clamp, is not a mere evaporation or volatilization of the metal, but a projection of molecules in straight lines in every direction. The trajectory of the molecules will be interfered with in some directions by the carbon filament; and hence result lines and places of no deposit which are molecular shadows of the loop. On every other part of the glass the molecules will impinge and adhere, forming a metallic coating. From the facts that the free paths of the molecules differ in length, and that the clamp is much nearer to the neck of the lamp than to the crown, it follows that a much larger proportion of the scattered molecules strike the glass near the neck, and the thickness of the deposit is therefore a measure of the proportion of molecules which have a free path, equal to the distance of that part of the envelope from the scattering point. Curiously enough the line of no deposit, or shadow of the loop, is not always seen in copper-deposited lamps. This may be because the scattering is going on from both clamps, and therefore the shadow on one side is covered up by the shower from the clamp on that side. It has been noticed in one or two cases that small tufts of carbon are seen on one clamp, and that when a well-defined shadow exists on that side, this seems to indicate that the shower of copper molecules has been partly stopped by the opposite clamp, which has therefore acted like a target and become encrusted with a proportion of the molecules shot at it.

With respect, next, to carbon deposits. Every one knows the appearance of a lamp after it has been burning for some time or overburnt: it is clouded with smoke-like deposit. In nearly all cases of copper deposit the molecular shadow exists, but it is not nearly so often seen in the case of carbon deposits. After many observations it was found that the molecular shadow of the filament, or line of no deposit, could be formed by suddenly raising the filament to a very high temperature, as for instance by placing a 50-volt lamp for an instant on a 100-volt circuit; whereas when the deposit of carbon takes place slowly, and as it were in the natural way, the lamp exhibits only a general smokiness but no line. Again, it has been found that when a carbon filament is cut sharply through at one point, caused by excessive temperature at one spot,

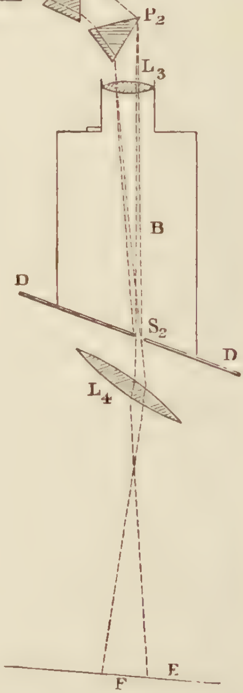
there is very frequently a sharply marked line of shadow of the loop on the side of the envelope farthest removed from the fracture. These facts seem to indicate that in normal use, when the lamp is not being pressed beyond the electromotive force at which it was intended to be used, there is a general evaporation of carbon going on from all parts of the loop, and these molecules, being projected with no abnormal velocity, probably collide with molecules of residual air a large number of times before they reach the walls of the envelope, and thus get their trajectories very much changed in direction. In this case the result would be to cause an irregular deposit of molecules of carbon on the glass envelope. But if we suppose a sudden or very excessive temperature to be given to part or the whole of the filament, this may cause a very violent projection of molecules of carbon from the filament; and these would pass outwards in straight lines, and a far larger proportion would reach the envelope in the direction in which they were first projected. This would then cause a deposit on all parts except those shielded by the loop; and in the case when such violent projection went on from all parts of the loop, as when a lamp is overheated, it is easily seen that parts of the envelope not lying exactly in the plane of the filament would receive twice as much deposit as those exactly in the plane. In most cases of carbon deposits the lamps which give the best shadows are those made with single loop, but it has also been observed on Swan lamps with double twist. By making lamps with clamps of various metals, it might be possible to obtain metallic films of various kinds. Interesting magneto-optic phenomena might perhaps present themselves in the case of transparent iron films, if they could be obtained.

XXIII. *The Production of Monochromatic Light, or a Mixture of Colours, on the Screen.* *By* Capt. W. de W. Abney, *R.E., F.R.S.**

For some time past I have been making experiments on the illuminating power of various sources of light, and it became necessary in some investigations to produce fair-

* Read June 27, 1885.

sized patches of different monochromatic, and combinations of monochromatic lights, upon a screen, all other colours being absent. To obtain this result I had recourse to a modification of Clerk-Maxwell's arrangement, as used for colour-mixing. By his plan slits were inserted at different parts of the spectrum as formed by an ordinary spectroscope. These slits were then illuminated by light reflected from a white screen, and the prism was viewed through the slit of what is ordinarily the collimator. The prism was then seen to be coloured

with light from those rays which would have fallen on those slits had the spectroscope been used in the ordinary manner. In this arrangement only one observer could be utilized at one time, and my object was to allow several observers simultaneously to view the colour. In order to effect this the following apparatus was employed:—A collimator C, the aperture of the lens L_2 of which was $1\frac{1}{2}$ inches, and the focal length about 12 inches, was employed. On the slit S_1 was cast an image of the source of light A by means of the condensing lens L_1. This was of such an aperture as entirely to fill the collimating lens L_2 with the rays entering through the slit.

Two prisms, P_1 and P_2, of $2\frac{1}{2}$ inches by $1\frac{3}{4}$ inch side, and of angles of 62°, gave the necessary dispersion to the parallel beam, from the collimator. The rays were brought to a focus by means of the lens L_3, of about 14 inches focal length, on to the screen belonging to a camera, B. This screen was placed at an angle with the axis of the lens L_3 as shown, so that a fair focus of every visible ray was obtained upon it. (It may be worth mentioning that a hair placed across the slit or a

little particle of dust is a good means of obtaining a focus when Fraunhofer or bright lines are not observable. The black streak produced by it should be sharp along the whole of the spectrum.) A card, D D, with a slit S_2 or slits cut in it, replaced the ordinary dark slide, and, by moving it along the spectrum, any colour or colours can be allowed to pass. Before using the apparatus the whole of the spectrum was caused to fall on a convex lens, L_4, of about 24 inches focal length and about 5 inches diameter. This collected the dispersed beam of light, giving an enlarged image, F, of one surface of one of the prisms on a screen, E. By placing this lens at an angle with the axis of the lens L_3, the blue and red fringes can be made to disappear almost entirely, and a practically white patch of light is seen on the screen E.

I may say that the lenses used are white flint of medium density and almost colourless, even in great thickness.

When the adjustments are complete, as the slit is moved along the spectrum every patch of colour or colours will successively occupy the same position on the screen and have the same area very nearly. We thus can have patches of monochromatic light of any colour or combinations of any colours, all other colour being absent.

I have also obtained the same results by substituting mirrors for all the lenses and a reflecting-grating for the prisms; but I do not see any particular advantage in this plan, as the white light is more tinged (with the colour of the metal) than when prisms and lenses of white glass are employed.

When the source of light is the arc light, if an image of the crater of the positive pole be thrown on the slit S_1 of the collimator, the intensity of the light is such (when the slit is fairly open) that the patch of nearly pure light may be made 1 foot square, and yet be sufficiently brilliant to be seen by a fairly large audience, and for an ordinary lecture-room it is very effective. The mixture of colours to imitate any colour in the spectrum may be shown by placing a narrow slit in a small card in the colour required to be imitated, and fixing in front of it and in contact with it a portion of a cylindrical lens, the axis of the cylinder being of course parallel to the slit. This throws the image of the particular colour to be observed at one side of the image that would be

obtained were the cylindrical lens absent, and any amount of deviation can be given the patch by using the different parts of the lens. Thus the greater the deviation required the nearer to the margin of the lens the part of it employed should be. In other words, the cylindrical lens acts as a series of prisms of varying angles. To obtain mixtures of colours to correspond to the deviated patch, movable slits, and capable of being narrowed or widened, are placed on each side of the fixed slit. By this plan two patches of light of equal size and equal intensity can be readily produced. When measurements are to be obtained, scales are attached to the various slits, by which any part of the spectrum can be identified; and the widths of the slits are measured by a gauge.

Since this apparatus was described I have referred to a paper by Helmholtz, which appeared in Poggendorff's *Annalen* in 1855, in which one of the methods he used for the combination of coloured light to produce white light is described. The general principle he adopted is the same as that described above; but in several important details the latter differs considerably from Helmholtz's apparatus. For instance, the apparatus now described is suitable for the comparison of colour-mixtures with monochromatic light of any colour and for their exhibition on the screen for lecture-purposes, and an illumination is secured which is very largely in excess of that usually obtained. In a paper read before the Physical Society (Phil. Mag. June 1885) Lord Rayleigh shows how a monochromatic image of an external object may be seen by placing a concave lens immediately behind the slit of the spectroscope of such a power as to throw an image of that object on the prism. I have found that by altering the distances apart of the collimating lenses and viewing lens, a monochromatic image of the sun may be thrown on the screen. If such an image be coloured with the light of the blue or violet hydrogen lines, it should be possible to photograph the solar prominences *en bloc*. I may mention that the apparatus as described was employed in two Cantor Lectures at the Society of Arts in the beginning of April, but without describing it in detail.

I am at present engaged in using this apparatus for investigating some phenomena existing in colour-blindness, and obtaining curves of illumination of different lights, and also

in some photographic researches. These results are not yet ripe for publication; but I have thought it might be well to publish the method employed, as it is one of great convenience, and very easily carried out by any one who has a spectroscope and a photographic camera.

XXIV. *On the Thermoelectric Position of Carbon.* *By* JOHN BUCHANAN *.

[Plate II.]

IN the very interesting paper read by Dr. J. A. Fleming before this Society on March 14, 1885, whilst discussing the question of the life of incandescent lamps, the author remarks that quite a large proportion of the carbon filaments are found to break at the negative end, that is near the point where the current passes from carbon to platinum. It seemed to me not improbable that the negative end of the carbon might be subjected to a heating action due to the operation of the "Peltier effect." The local excess of temperature thus produced might possibly account for the observed result. In any case the determination of the position of the carbon line on the thermoelectric diagram was of interest. I am not aware that this has been done before.

Result.—For the specimen of carbon I have tried, the Thomson effect is of the same sign as in copper, and about twice the value for that metal given by Prof. Tait, as quoted in Everett's "Units and Physical Constants," § 186. The thermoelectric power of carbon is given by my experiments,

$$e_c = -390 - 1{\cdot}87t \text{ C.G.S. units}, \quad . \quad . \quad . \quad (1)$$

where t denotes, as usual, the mean temperature of the junctions. The neutral point of carbon with lead is therefore about $-209°$ C.

Thermo-couple of Platinum-Carbon.—As I have mentioned, the series of experiments described below were undertaken with the object of finding the magnitude of the Peltier effect in incandescent lamps. I therefore examined specially the behaviour of a thermoelectric couple of platinum-carbon.

* Read June 27, 1885.

The platinum was a piece of ordinary commercial wire procured from Messrs. Johnson and Matthey. The carbon was in the form of rods 12 millim. diam., such as are made for use in arc lamps. The direction of the current in such a couple is from platinum to carbon across the hot joint. The thermo-electric power at the mean temperature t is

$$e_{pt-c} = +566 + 3{\cdot}94t \text{ C.G.S. units.} \quad . \quad . \quad (2)$$

Due, therefore, to the "Peltier effect," heat will be generated at the negative end of the carbon filament of an incandescent lamp when the current is passing. We can now calculate what proportion the heat thus generated locally bears to the whole quantity of heat generated in the filament.

If T denote the neutral point of a thermo-couple, then the Peltier effect for the absolute temperature θ at one joint is given by

$$\pi = (K_1 - K_2)(T - \theta)\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where K_1 and K_2 are the numbers that express for each material the ratio that the Thomson effect bears to the absolute temperature. (See Tait's 'Heat,' § 415.)

Hence for a platinum-carbon couple,

$$\pi = 3{\cdot}94\ (144 + \theta)\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As a specific example, take the case of a 100-volt lamp, with the filament at a temperature of 2400° C. We get the ratio

$$\frac{\text{Heat due to Peltier effect}}{\text{Whole heat in filament}} = \frac{3{\cdot}94 \times 2673(144 + 2400)}{100 \times 10^8},$$

$$\text{,,} \qquad = \frac{2{\cdot}7 \times 10^7}{10^{10}},$$

$$\text{,,} \qquad = {\cdot}0027.$$

The local heating at the negative end of the filament is therefore only about one quarter per cent. of the whole heat. This is too small to have any appreciable influence on the life of the lamp. It does not appear therefore that the Peltier effect accounts for the giving way of the carbon-filament at one end rather than at the other. In the course of these experiments one phenomenon was forced on my attention, the details of which are given below. It seems that con-

tinuous heating alters the thermoelectric properties of carbon. This alteration must be the result of molecular change in the material. That this has any bearing on the destruction of the filament that ensues, by keeping it for a long time at a high temperature, my experiments are not extended enough to decide.

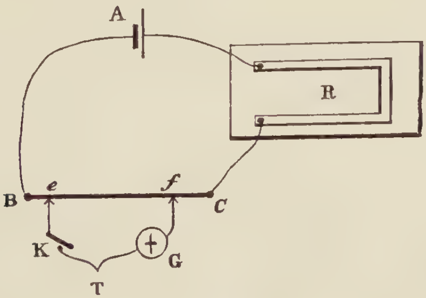
Experimental Details.

The E.M.F. at various temperatures was determined by the null method known as Poggendorff's.

The primary circuit contained a constant cell A, a graduated wire BC, and a box of resistance-coils R.

On the graduated wire were placed sliding pieces *e* and *f*, which served as the terminals of the secondary circuit. In the secondary circuit were a galvanometer G, and the thermo couple T whose E.M.F. was to be measured, and a key K.

Fig. 1.



The arrangement of the apparatus used in the platinum-carbon experiments has now to be described.

Three rods of carbon of 1·2 centim. diameter, such as are manufactured for use in arc-lamps, were taken. One of these was thinned down into a conical form at the end destined to go into the hot bath. This end, and that of another rod intended to go into the cold bath, were electroplated with a thin shell of copper. To this copper shell were soldered the platinum wires, whose behaviour with the carbon I wished to examine. These two rods were then placed vertically and clamped in position with coppered ends dipping into their respective baths. The upper ends of these carbon rods were cut off square and the third rod laid horizontally, so as to

form with the vertical rods the third side of a vertical rectangle.

To ensure good contact one end of this third rod was bound by a number of turns of clean iron wire to the upper end of the rod whose lower end dipped into the cold bath. The other end of this third rod rested on the top of the rod the lower end of which dipped into the hot bath. The surfaces of contact were here scraped flat and kept pressed together by a weight of 3 or 4 pounds.

The platinum wires that formed the other element of the thermo-couple were of ordinary commercial material, as was mentioned above.

The galvanometer used in the secondary circuit is a very delicate mirror instrument of about $\frac{1}{4}$ ohm resistance.

The cell used in the primary circuit as a standard was a Daniell. The graduated wire (BC in fig. 1) was of German silver.

The baths, both hot and cold, were oil-baths.

The ends of the platinum wires of the thermo-couple that were exterior to the baths were joined by binding-screws to copper wires. These joints were insulated from one another by several layers of calico, and then tightly wrapped up together. Thus in the secondary circuit the only exposed contacts of dissimilar conductors were those of the copper wires joined up with the brass binding-screws of the key, of the galvanometer, and of the sliding piece on the graduated wire. During the experiment, care was taken to screen these exposed contacts as much as possible from external radiation. Moreover, all the apparatus was set up the night before, so that on the days of the experiments no metal joints whatever in the secondary circuit were touched by hand.

Some preliminary experiments I had made showed the necessity for adopting the arrangements just described. The results of these preliminary trials exhibited very curious irregularities, not altogether got rid of even by those latest arrangements. By using the precautions detailed above, I ensured, however, that the place of any disturbances that might come into play should be located with certainty in the thermo-joints under examination.

The proper amount of resistance to be inserted in the

primary circuit having been determined beforehand, the primary circuit was closed. The current was allowed to flow during the whole time the experiment lasted. The temperature of the hot bath was raised very slowly up to the highest point reached; then as slowly lowered again. Frequent readings of the thermometers in the hot and cold baths were taken. Simultaneously were noted the positions of the movable sliders on the graduated wire, for which no deflection was shown by the galvanometer on depressing the key in the secondary circuit.

When a temperature reading was intended to be taken, the temperature was kept as steady as possible for $\frac{1}{4}$ to $\frac{1}{2}$ a minute, accompanied with constant stirring of the hot bath. In this way a series of corresponding readings of temperature and of distances on the graduated wire were obtained. The results were plotted out, taking centimetres of the graduated wire as ordinates, and temperatures of the hot bath as abscissæ. A regular curve was then drawn amongst the points thus obtained, so as to give as nearly as could be judged the mean of the observations. The curves A, B, C (Plate II.) were obtained in this way. The scales for these curves are not quite the same. Details are given below. The curves A and B were obtained on successive days.

The want of regularity in the individual readings, after all the precautions taken, I considered could only be due to the properties of the carbon. Partly to satisfy myself that no essential precaution had been overlooked, however, and partly to test an idea I formed as to the cause of the irregularities, the apparatus was set up again about a month later. Curve C gives the results of the observations. The heating of the hot joint gave the curve to the left hand; the subsequent cooling gave the right-hand curve. These curves have not a point of intersection at their upper ends shown in the diagram (Plate II.), because the temperature was intentionally raised to a point higher than that for which a reading on the graduated wire could be obtained, before cooling down was begun.

Now, as $4\frac{1}{2}$ hours were given to the observations, the heating and cooling took place very slowly indeed. And as a stirrer was kept almost continuously in operation in the hot bath, the lagging of the thermometer behind the thermo-

joint must have been very small. I believe that the difference between the curves obtained by heating and by cooling is partly due to change taking place in the properties of the carbon as the temperature changes. Bearing on this there is an observation I made. Having calculated the neutral point of a carbon-iron couple as about $+208°$ C., a glycerine bath was used to verify this result. Having raised the temperature to about 290° C. and cooled again to 220° C. several times, I found the E.M.F. of the carbon-iron couple rose gradually, until at the time of stopping the experiment the maximum E.M.F. had increased by more than 50 per cent. As is well known, a thermo-couple reaches a maximum E.M.F. when the temperature of one joint is that of the "neutral point." It was this maximum that was found to increase with the time during which heat was applied.

The conclusion is, that the thermoelectric properties of carbon alter with temperature. Principally for this reason I did not deem it of utility to begin a new series of observations, and by "loading" the hot joint with metal try to decrease the irregularities in the readings like those in curves A and B. Moreover, the results calculated from these curves agree as well as could be expected. Here are the details:—

Curve A.

Assuming the equation to the curve as

$$y=\mathrm{K}(x-a)\left(\mathrm{T}-\frac{x+a}{2}\right),$$

I find that $\mathrm{T}=-147°$ C., $\mathrm{K}=0{\cdot}00470$

satisfy best the observations as represented by the curve A.

x = temperature of hot bath,
a = " cold bath,
T = neutral point.

The agreement of calculated and observed values of y is exhibited by Table I.; these values, it will be recollected, represent centimetres of the bridge-wire. To calculate the E.M.F. of a carbon-platinum thermo-couple as given by curve A, we have the following data:—

Resistance of primary circuit . . . . . . = 303·6 ohms.
Observed E.M.F. of Daniell used . . . . = 1·03 volt.
Resistance of 1 centim. of the graduated wire = ·00246 ohm.

Denoting the E.M.F. required by E_A, we get

$$E_A = \cdot 00470 \times 1\cdot 03 \times 10^8 \frac{\cdot 00246}{303\cdot 6}(x-a)\left(147+\frac{x+a}{2}\right),$$

$$\therefore \quad E_A = 3\cdot 92(x-a)\left(147+\frac{x+a}{2}\right) \text{ C.G.S. units.}$$

Hence the thermoelectric power of the couple is

$$e_A = +577 + 3\cdot 92 \times t \text{ C.G.S. units,}$$

t denoting the mean temperature of the joints. The direction of the current would be from Pt to C across the hot joint.

Curve B.

Taking an equation to the curve of the same form as that just used, T $= -140°$ C. and K $= \cdot 00406$ best satisfy observation.

TABLE I.

x.	a.	y.	
		Calculated.	Observed.
30°	9·75°	15·9	15·8
40	9·82	24·4	24·2
50	9·85	33·4	33·4
60	"	42·9	43·1
70	"	52·9	53·0
80	9·9	63·2	63·4
90	"	74·2	74·1
100	"	85·5	85·1
110	"	97·4	97·7

TABLE II.

x.	a.	y.	
		Calculated.	Observed.
30°	9·6°	13·5	13·2
40	9·65	20·3	20·3
50	9·70	27·8	27·8
60	9·75	35·7	35·7
70	"	43·8	44·0
80	"	52·6	52·7
90	9·80	61·9	61·9
100	"	71·7	71·4
110	9·85	81·8	82·4
120	"	92·6	91·6

Table II. exhibits the agreement of the calculated and observed values of y when these constants are inserted in the

equation to the curve. To calculate E.M.F. (E_B), the data are the same as were used in the calculation of E_A, except that the resistance in the primary circuit was 259·6 ohms.

$$\therefore\ E_B = \cdot 00406 \times 1\cdot 03 \times 10^8 \times \frac{\cdot 00246}{259\cdot 6}(x-a)\left(140+\frac{x+a}{2}\right)$$

$$= 3\cdot 96(x-a)\left(140+\frac{x+a}{2}\right) \text{ C.G.S. units.}$$

Hence for the thermoelectric power (e_B) at the mean temperature t, we get

$$e_B = +555 + 3\cdot 96t \text{ C.G.S. units.}$$

The mean of e_A and e_B being denoted by e_{pt-c}, we get

$$e_{pt-c} = +566 + 3\cdot 94t \text{ C.G.S. units,}$$

the result quoted in equation (2) above.

Thermoelectric Power of Carbon.

In order to find the position of carbon on the thermoelectric diagram, I determined the line on this diagram of the platinum employed in the above experiments.

A strip of commercial lead, about 80 centims. long, had the platinum wires soldered to the ends. The general arrangement of the apparatus and the precautions used were similar to what have already been described above. Curve D shows the results of the observations; the ordinates and abscissæ being the same as in the curves A, B, C. It will be noticed that the observations lie well on the mean curve, thus showing that the arrangements were not defective in any essential point.

Assuming
$$y = K(x-a)\left(T-\frac{x+a}{2}\right)$$

as the equation to the curve, as above, I find that T = −85° C. and K = ·004815 give results agreeing best with observation. (See Table III.)

TABLE III.

x.	a.	y. Calculated.	y. Observed.
30°	13·1°	8·67	9·05
50	"	20·7	20·6
70	"	34·6	34·7
90	"	50·5	50·8
110	"	68·3	68·2
130	"	88·1	88·0

The data for calculation are :—

Resistance of primary circuit . . . . $=1001$ ohms.

Mean observed E.M.F. of the Grove cell employed . . . . $\Big\} = 1{\cdot}75$ volt.

Hence the E.M.F. of the lead-platinum couple and the thermoelectric power of platinum are, respectively,

$$E = {\cdot}004815 \times 1{\cdot}75 \times 10^8 \frac{{\cdot}00246}{1001}(x-a)\left(85+\frac{x+a}{2}\right);$$

$$\therefore\ E = 2{\cdot}07(x-a)\left(85+\frac{x+a}{2}\right) \text{ C.G.S units,}$$

$$\therefore\ e_{pt} = +176 + 2{\cdot}07t \text{ C.G.S. units.}$$

The current would be from Pt to Pb across the hot junction.

Using this value for e_{pt}, we find for the thermoelectric power of carbon

$$e_c = -390 - 1{\cdot}87t \text{ C.G.S. units.}$$

This is the result quoted in equation (1) above.

In the table of thermoelectric powers given by Everett ('Units and Physical Constants,' § 186) there are given

$$\text{for Zn,}\quad e_{zn} = -234 - 2{\cdot}40t,$$

$$\text{,, Ag,}\quad e_{ag} = -214 - 1{\cdot}50t.$$

The value for e_c shows that the place of carbon in the table is between zinc and silver. In the thermoelectric diagram it is easy to see that for temperatures below 50° C., the line for carbon lies below that for cadmium, taking the value for e_{cd} from Everett's table (*loc. cit.*).

Concluding Remarks.

The disintegration preceding complete destruction of the carbon filament in an incandescent lamp, described by Mr. W. H. Preece, F.R.S., in a paper read before the Royal Society on March 26, 1885, is doubtless the result of molecular changes in the structure of the filament produced by the continued maintaining of the filament at an extremely high temperature. In my experiments, keeping carbon at a moderately high temperature altered the molecular condition of this material, the alteration being manifested as a change in the thermoelectric power of the carbon.

Physical Laboratory, University College,
London, June 1885.

XXV. *On the Specific Refraction and Dispersion of Light by the Alums.* By J. H. Gladstone, *Ph.D., F.R.S.**

In the *Comptes Rendus* of November 17, 1884, there appears a paper by M. Charles Soret, in which he gives the refractive indices of a large number of crystallized alums. They were determined by the method of total reflection, and are measured for the lines of the solar spectrum *a*, B, C, D, E, *b*, F, and G. As at the same time M. Soret gives the specific gravity of the specimens examined, it is easy to calculate out the specific refraction and dispersion of these crystals, and it occurred to me that the observations might serve three purposes. They might test the truth of certain physical laws; they might arbitrate between myself and Kanonnikoff as to the refraction-equivalent of certain metals; and they would give values for indium and gallium, which have not hitherto been obtained. Through the kindness of M. Soret I have received his full paper†, with some further information, and observations on three additional alums not yet published, viz. the Rubidium Gallium, Rubidium Indium, and Cæsium Chromium alums.

In order to bring M. Soret's figures into comparison with my own, which are always based on the line A of the spectrum, it was necessary to reduce his figures accordingly. This was easily done, as the line A falls short of *a* by almost exactly the same amount as that one falls short of B. The following table gives the specific gravity of the selected crystals; the refractive indices (μ) for A calculated to the fourth place of decimals, and also those for G; the specific refraction for A, *i. e.* the index -1 divided by the density, $\left(\frac{\mu_A-1}{d}\right)$; the specific dispersion A to G, *i. e.* the difference between the specific refraction of these two lines, $\left(\frac{\mu_G-\mu_A}{d}\right)$; and the refraction-equivalent for A, *i. e.* the specific refraction multiplied by the

* Read June 27, 1885.

† "Recherches sur la Refraction et la Dispersion des Aluns crystallisés," *Archives des Sciences Physiques et Naturelles*, vol. xii. p. 553, and vol. xiii. p. 5.

atomic weight, $\left(P\frac{\mu_A-1}{d}\right)$. The general formula of the alums is $R_2, Al_2, 4SO_4, 24H_2O$; the aluminium being replaceable by indium, gallium, chromium, and iron.

Alum.	Specific gravity.	μ_A.	μ_G.	$\frac{\mu_A-1}{d}$.	$\frac{\mu_G-\mu_A}{d}$.	$P\frac{\mu_A-1}{d}$.
Ammonium Aluminium..	1·631	1·4542	1·4692	·2784	·0093	252·23
Sodium " ...	1·667	1·4342	1·4480	·2604	·0083	238·52
Methylamine " ...	1·568	1.4496	1·4636	·2867	·0090	267·68
Potassium " ...	1·735	1·4516	1·4661	·2603	·0083	246·81
Rubidium " ...	1·852	1·4513	1·4662	·2437	·0080	253·69
Cæsium " ...	1·961	1·4536	1·4682	·2313	·0074	262·31
Thallium " ...	2·257	1·4914	1·5108	·2177	·0086	278·34
Ammonium Chromium...	1·719	1·4781	1·4959	·2781	·0104	265·94
Potassium " ...	1·817	1·4754	1·4931	·2616	·0098	261·22
Rubidium " ...	1·946	1·4756	1·4932	·2444	·0090	266·69
Cæsium " ...	2·043	1·4753	1·4928	·2326	·0086	275·50
Thallium " ...	2·386	1·5158	1·5381	·2161	·0092	286·90
Ammonium Iron	1·713	1·4783	1·4998	·2792	·0126	269·15
Potassium "	1·806	1·4757	1·4960	·2634	·0112	265·03
Rubidium "	1·916	1·4763	1·4970	·2486	·0108	273·21
Cæsium "	2·061	1·4772	1·4984	·2315	·0103	275·95
Thallium "	2·385	1·5155	1·5411	·2161	·0108	288·85
Rubidium Indium.........	2·065	1·4586	1·4740	·2221	·0074	269·63
Rubidium Gallium	1·962	1·4606	1·4758	·2348	·0077	264·43

Messrs. Topsoe and Christiansen* have also published the refractive indices of three alums for the lines C, D, and F; and as they have given the specific gravity, their observations are available for the same purpose. The index for A has been calculated from these data.

Alum.	μ_A.	μ_C.	$\frac{\mu_A-1}{d}$.	$P\frac{\mu_A-1}{d}$.
Potassium Iron Sulphate	1·4751	1·4783	·2597	261·37
Ammonium Iron Sulphate	1·4789	1·4821	·2786	268·56
Potassium Aluminium Seleniate	1·4748	1·4773	·2409	272 98

How far do these figures support the former conclusion, that a salt has the same specific refraction whether in a solid form or in solution?

* "Krystallografisk-optisk Undersoegelser," *Det K. Danske Videnskabernes Selskabs Skrifter*, 1873, p. 622.

For this purpose determinations were made of the refraction for A in aqueous solutions of the first two alums in M. Soret's list. Deducting the amount due to the solvent, the following values were arrived at :—

	Dissolved.	Crystallized.
Ammonium Aluminium alum . .	·2780	·2784
Sodium Aluminium alum . . .	·2613	·2604

These numbers are as close as two different specimens of the same salt, even if they were in the same condition, are likely to be. It did not seem worth while to obtain additional proof of a law which has already been established by many cases; not only by my previous observations, but also by those of Topsoe, Bedson, and Kanonnikoff.

Do these figures confirm the law that the refraction-equivalent of a compound body is the sum of the refraction-equivalents of its components?

The alums may be regarded as a compound of the sulphates of two metals of different kinds with 24 molecules of water. Now water in the uncombined state has the refraction-equivalent of 5·926; and in regard to the sulphates we have the following data :—

Ammonium sulphate, $(NH_4)_2SO_4$, 39·3. The mean of five determinations made by myself gives 39·35 *: Kanonnikoff gives 39·27 †.

Sodium sulphate, Na_2SO_4, 26·6. Kanonnikoff gives 26·02.

Methylamine sulphate, $(NCH_6)_2SO_4$, 54·5; *i.e.* ammonium sulphate with the addition of $2CH_2$, or 15·2.

Potassium sulphate, K_2SO_4, 32·4. The mean of five determinations gave me 32·6: Kanonnikoff gives 32·22. It may be estimated at 32·3 from Topsoe and Christiansen's determinations of the crystallized salt.

Rubidium sulphate, Rb_2SO_4, 41·3. This is Kanonnikoff's determination, which I prefer to my own made in 1869.

Cæsium sulphate, Cs_2SO_4, 55·3. Also Kanonnikoff's.

Being not content with my old observations on the sulphates of the trivalent metals, I have recently determined them afresh, with the following results :—

Aluminium sulphate, $Al_2(SO_4)_3$, 70·5.

* Four of these are given in my paper in the Phil. Trans. 1869, p. 9.

† Journal of the Russian Physico-Chemical Society, 1884, p. 119.

Chromium sulphate, $Cr_2(SO_4)_3$, 82·5 ; the result of old and new observations.

Ferric sulphate, $Fe_2(SO_4)_3$, 89·1 ; the mean of old and new observations.

It is evident that on adding together

Ammonium sulphate . .	39·3
Aluminium sulphate . .	70·5
24 Water	142·2
We obtain	252·0

In this way the second column of the following table has been calculated :—

Substance.	Refraction-equivalent.		
	Calculated.	Observed, and reduced to A.	
		Soret.	Topsoe and Christiansen.
Ammonium Aluminium alum......	252·0	252·2	
Sodium ,, ,, ...	239·3	238·5	
Methylamine ,, ,, ...	267·2	267·7	
Potassium ,, ,, ...	245·1	246·8	
Rubidium ,, ,, ...	254·0	253·7	
Cæsium ,, ,, ...	268·0	262·3	
Ammonium Chromium alum	264·0	265·9	
Potassium ,, ,, ...	257·1	261·2	
Rubidium ,, ,, ...	266·0	266·7	
Cæsium ,, ,, ...	280·0	275·5	
Ammonium Iron alum................	270·6	269·1	268·6
Potassium ,, ,, ...	263·7	265·0	261·4
Rubidium ,, ,, ...	272·6	273·2	
Cæsium ,, ,, ...	286·6	276·0	

The agreement between the results calculated and found is as near as might be expected, except in the case of cæsium. It confirms the general law, as the variations only in one instance amount to as much as 1 per cent., and are sometimes plus and sometimes minus. There is little doubt that the cæsium, in one set of observations or the other, was impure : an old determination of mine, from the chloride, would give figures lower than Soret's.

Do these data afford us the means of determining the refraction-equivalents of the elements with more exactness than heretofore ? It is evident that in the series of aluminium

alums the metal having the smallest refraction-equivalent is sodium, and that the rest follow in the order—potassium, ammonium, rubidium, methylamine, cæsium, and thallium ; the same order is preserved in the chromium and iron alums as far as they extend. This agrees with the order previously determined both by myself and Kanonnikoff; but when we look more closely into the matter it is evident that the figures are not very exact. Thus, in the aluminium series the difference between $2NH_4$ and $2K$ is 5·42 ; but in the chromium series it is only 4·72, and in the iron series 4·12, or 7·19 according to Topsoe. The values of potassium deduced from this would vary considerably : assuming the value of NH_4 to be 11·1, it might be either 8·4, 8·7, 9·0, or 7·5 ; which are wider differences than between my old estimation, 8·1, and Kanonnikoff's recent independent determination, 7·75. This will not be wondered at when it is remembered that all experimental errors are accumulated on these residual numbers. The optical determinations of Soret are so uniform and exact as to inspire the greatest confidence ; but he is not satisfied with the specific gravities. Errors may also arise from impurity of the salt, or want of homogeneity in the crystal. An aqueous solution is probably a more uniform substance than a hydrated crystal, and better fitted for the purpose of determining optical equivalents.

On this account any determination of the refraction of indium and gallium made from these alums must be open to considerable question : the rubidium compounds of these metals, however, are believed by Soret to be fairly pure salts, and we can compare them with three other alums of rubidium. It would appear from the first table that indium has the value of aluminium +8·0, or of chromium +1·5, or of iron −1·8 ; and, similarly, that gallium has the value of aluminium +5·4, or of chromium −1·1, or of iron −4·4. Now aluminium sulphate has already been estimated at 70·5, chromium sulphate at 82·5, and ferric sulphate at 89·1, while the value of SO_4 is held both by Kanonnikoff and myself to be 17·0. We may therefore deduce the following refraction-equivalents :—

Aluminium	9·7
Chromium	15·7
Iron	19·0

and :—

	From Aluminium Salt.	From Chromium Salt.	From Iron Salt.
Indium	17·7	17·2	17·2
Gallium......	15·1	14·6	14·6

From the mean of the above the following constants may be derived :—

	Atomic weight.	Specific refraction.	Refraction-equivalent.
Indium	113·6	·1532	17·4
Gallium..................	69·8	·2120	14·8

These numbers can only be looked upon as approximate.

Turning to the matter of dispersion.—It has already been shown that the refraction-equivalent of an alum is the sum of the refraction-equivalents of its constituents for the line A. If this law holds good equally for the more-refrangible part of the spectrum, it follows that the dispersion-equivalent $\left(P\frac{\mu_G - 1}{d} - P\frac{\mu_A - 1}{d}\right.$, or, which is the same thing, $\left.P\frac{\mu_G - \mu_A}{d}\right)$ of an alum is the sum of the dispersion-equivalents of its constituents. The data by which this can be tested are not so numerous or so trustworthy as in the former case, but the following may be accepted.

The dispersion-equivalent for water . . . . 0·212
" " aluminium sulphate 2·40
" " ammonium sulphate 1·33
" " sodium sulphate . 0·83

from which may be deduced :—

Dispersion-equivalent of	Calculated.	Observed.
Ammonium alum............	8·82	8·40
Sodium alum	8·32	7·65

Though these figures are tolerably accordant, it will be seen that those in the first column are decidedly higher than those deduced from Soret's measurements. The differences are about 5 and 8 per cent. respectively; but there are known sources of error in experiment which may affect the first place of decimals.

The dispersion-equivalents of the different alums may be thus tabulated :—

	Dispersion-equivalents of the Alums.				
	Aluminium.	Chromium.	Iron.	Indium.	Gallium.
Ammonium salt ...	8·40	9·91	12·11		
Sodium ,,	7·65				
Methylamine ,,	8·47				
Potassium ,,	7·92	9·73	11·31		
Rubidium ,,	8·36	9·87	11·86	8·98	8·73
Cæsium ,,	8·44	10·15	12·28		
Thallium ,,	10·98	12·13	14·45		

It is evident at once :—

First. That the differences due to the replacement of one metal by another are very considerable; more considerable in proportion than the differences in the case of the refraction-equivalents.

Secondly. That the different compounds of the alkalis preserve the same order, and nearly the same proportion, in the aluminium, chromium, and iron series: the order is thallium far the highest, methylamine, cæsium, ammonium, rubidium, potassium, and sodium lowest. This is the same order which may be deduced from old observations on sulphates, nitrates, chlorides, and acetates.

Thirdly. That the order of the other metals is iron far the highest, chromium, indium, gallium, and aluminium lowest. This is also in accordance with observations on the simple sulphates of those previously examined.

Our knowledge on this part of the subject is not yet sufficiently advanced to determine the dispersion-equivalents of the separate elements.